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ON THE NATURE OF AQUEOUS STRONG ACID SOLUTIONS  
BY  
EDWARD BROCK ROBERTSON, B.SC.  
  
A THESIS  
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
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UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled ON THE NATURE OF AQUEOUS STRONG ACID SOLUTIONS submitted by Edward Brock Robertson, B.Sc. in partial fulfilment of the requirements for the degree of Doctor of Philosophy.





### ABSTRACT

A model has been proposed which is capable of accounting quantitatively for the acidity of aqueous solutions of sulfuric, perchloric, hydrobromic, hydrochloric and nitric acids in terms of hydration of the proton. Calculations were performed over the concentration ranges for which data was available in the literature; in the case of sulfuric acid from 0.1 to 1000 m. A computer programmed model which considered up to four proton hydrate species co-existing in solution was found to be more satisfactory than a model which considered only one proton hydrate species. In concentrated acid, the single species model required more water for proton hydration than the solution contained, whereas the multi-species model always gave values of the hydration number which were physically possible.

The acidity was in general taken to be given by the Hammett acidity function, but some calculations were performed using other acidity functions. There is not sufficient data available at present to apply a proper correction for the activity coefficients of the indicators, but the effect of the correction was considered qualitatively for the system sulfuric acid - water using the Hammett acidity function.

The use of Raoult's law in a form which considered the true chemical species present rather than the stoichiometric composition gave reasonable values of the hydration number of the electrolyte at acid concentrations greater than about 3 to 4 m. The failure of Raoult's law at low acid concentrations has been interpreted to be caused by the



neglect of consideration of the structure of the solvent. Specifically, the "flickering cluster" model for pure water has been used, and it is postulated that no clusters exist at acid concentrations greater than about 3 m.

An apparent maximum was observed in the proton hydration number as a function of acid concentration in sulfuric acid. It was shown that the maximum is not caused by hydration of the indicators nor the activity coefficients of the indicators, but may arise from changes in the activity coefficient of the proton caused by some factor other than hydration.

The values of the hydration number predicted by Raoult's law were found to be considerably smaller than those predicted from the acidity function, even after correction for the activity coefficients of the indicator pair. The source of the discrepancy is not known. The values of the apparent proton hydration number calculated from the acidity function were found to be larger than might be expected in dilute solution, suggesting that the activity coefficient of the hydrated proton also contributes to the acidity.





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# LIST OF PRINCIPAL SYMBOLS

A	Total concentration of anion hydrate species.
B	Basic form of the indicator used to determine the Hammett acidity function.
$BH^+$	The conjugate acid of B.
C	Concentration in molar units if concerned with specific numbers; also used as concentration in unspecified units in the theoretical section. If no subscript is used, refers to the stoichiometric molarity of acid.
$H_O, H_O'''$ , $H_R, H_-$ , and G	Logarithmic forms of the acidity functions based on primary aniline, tertiary aniline, triarylcarbinol, cyanocarbon and thiazine indicators, respectively.
P	Total concentration of proton hydrate species.
Q	Total concentration of water of proton hydration.
$R^+$	Carbonium ion formed by the ionization of ROH
ROH	Basic form of the indicator used to determine the $H_R$ acidity function.
a	Activity of the species indicated by the subscript.
d	Hydration number of ROH.
e	Hydration number of $R^+$ .
f	Activity coefficient of the subscripted species; takes the reciprocal units of the corresponding concentration.
g	The integral number of moles of water of hydration attached to one mole of the anion of an acid.
$\bar{g}$	The average apparent hydration number of the anion.
$\bar{g}''$	An approximation to $\bar{g}$ (Högfeldt's model).
$h_O, h_R$	The non-logarithmic forms of the $H_O$ and $H_R$ functions.
h	The true hydration number of the proton.
i	Hydration number of B.





$j$	Hydration number of $BH^+$ .
$\underline{k}$	The average apparent hydration number of the electrolyte.
$\underline{k}'$	An approximation to $\underline{k}$ (Högfelt's model).
$m$	The molality of the subscripted species; if no subscript is used, refers to the stoichiometric molality of acid.
$n$	The integral number of moles of water of hydration associated with one mole of proton.
$\underline{n}$	The average apparent hydration number of the proton.
$\underline{n}''$	An approximation to $\underline{n}$ (Högfelt's model).
$\underline{n}_S, \underline{n}_R, \underline{n}_H, \text{ and } \underline{n}_C$	$\underline{n}$ as obtained from the total stoichiometric water concentration, from the use of Raoult's law, from the idealized single species acidity function equation, or from the computer calculations.
$\alpha$	The degree of dissociation of an acid.



# ON THE NATURE OF AQUEOUS STRONG ACID SOLUTIONS

## INTRODUCTION

In the elucidation of the nature of concentrated electrolytic solutions, one particular type has received special attention, namely aqueous solutions of strong acids. There are probably two main reasons for this: concentrated solutions of strong acids are particularly important in mechanistic studies using the Zucker-Hammett<sup>1</sup> and similar approaches<sup>2</sup>; and secondly the very practical consideration that these solutions possess an additional property, their acidity, which should yield additional information about them.

A convenient measure of the acidity is the Hammett acidity function,  $h_o$ , defined as<sup>3</sup>

$$h_o = a_{H^+} f_B / f_{BH^+} = C_{H^+} f_{H^+} f_B / f_{BH^+} \quad (1)$$

where  $a_{H^+}$  is the activity,  $C_{H^+}$  the concentration, and  $f_{H^+}$  the activity coefficient of the proton; and  $f_B$  and  $f_{BH^+}$  are the activity coefficients of the indicator B and its conjugate acid  $BH^+$ . However, there has long been evidence (reviewed in reference (4)) that in aqueous solution the proton exists as the oxonium ion,  $H_3O^+$ , and it has been suggested that thermodynamicists could replace  $H^+$  by  $H_3O^+$  with at least equal logic<sup>5, 6, 7</sup>.

Equation (1) would then become

$$h_o = C_{H_3O^+} f_{H_3O^+} f_B / a_{H_2O} f_{BH^+} \quad (2)$$

where  $a_{H_2O}$  is the activity of water. Equation (2) shows that at least



part of the increase in acidity with increasing acid concentration is caused by the simultaneous decrease in the activity of water.

There is nothing to prevent further hydration of the oxonium ion: in fact, it had been suggested as early as 1920.<sup>8</sup> About ten years ago, Wicke, Eigen and Ackermann<sup>4</sup> studied the partial molal heat capacity and partial molal volume of dilute aqueous HCl, and arrived at a physical model of a double layer hydration of the oxonium ion. At infinite dilution, their model gave a primary hydration number of four, and a secondary temperature dependent hydration number of 3.7 to 1.5 over the range 0 to 100°C. The average hydration bond energy of the secondary water molecules was estimated to be 4.9 kcal./mole. The inner shell was stable over the temperature range studied. Glueckauf<sup>9</sup> obtained a hydration number of four for the proton from activity coefficient studies and from measurements of the uptake of water by acidic ion exchange resins. Since that time, numerous investigators have obtained the same or similar values (cf. reference (10)).

#### The Bascombe and Bell Model.

Bascombe and Bell<sup>11</sup> attempted quite successfully to predict  $H_0$  ( $= -\log h_0$ ) in moderately concentrated aqueous strong acids from a model based on the tetra-hydrated proton. They considered the problem from two points of view involving slightly different assumptions.

By analogy with equations (1) and (2), the Hammett acidity function can be written as

$$h_0 = C_{H^+(H_2O)_n} f_{H^+(H_2O)_n} f_B / a_{H_2O}^n f_{BH^+}$$





or 
$$-H_o = \log C_{H^+(H_2O)_n} - n \log a_{H_2O} + \log (f_{H^+(H_2O)_n} f_B / f_{BH^+}) \quad (3)$$

where  $h_o$  refers to the equilibrium



Here,  $n$  is the hydration number of the proton,  $C_{H^+(H_2O)_n}$  is the concentration of the hydrated proton,  $a_{H_2O}$  is the activity of water, and the  $f$ 's are the activity coefficients of the species indicated by the subscripts.<sup>a</sup> They assumed that the concentration of the hydronium ion was equal to the stoichiometric molar acid concentration,  $C$ , and that to a first approximation  $f_{H^+(H_2O)_n} = f_{BH^+}$ . Hence, equation (3) can be written

$$\begin{aligned} -H_o - \log C + n \log a_{H_2O} &= \log f_B \\ &= AC \end{aligned} \quad (5)$$

if the Setschenov equation<sup>12</sup> is valid for  $f_B$ .  $A$  is an empirical constant that indicates the amount of solute - solvent interaction. Plotting the left hand side of equation (5) vs.  $C$ , with  $n = 4$ , gave  $A = 0.07$ ,  $0.1$  and  $0.1$  for  $HCl$ ,  $HClO_4$  and  $H_2SO_4$ , respectively. These are reasonable values to expect for the salting - out of organic molecules by strong acids<sup>12</sup>, and hence Bascombe and Bell concluded that  $n = 4$  was an acceptable value for the hydration number.

The second approach is based on equation (3) written in the alternative form

<sup>a</sup> Here and in the following discussions, the notation of the original authors has been changed to correspond to the notation used in the present work.



$$-H_o = \log C - n \log C_{H_2O} + \log(f_{H^+}(H_2O)_n f_B / f_{H_2O}^n f_{BH^+}) \quad (6)$$

where  $C_{H_2O}$  is the molar concentration of water and  $f_{H_2O}$  is the molar activity coefficient of water. It was again assumed that  $f_{H^+}(H_2O)_n = f_{BH^+}$ , and further that  $f_B = f_{H_2O}^n$  — i.e. that the last term in equation (6) vanishes. Bascombe and Bell took  $C_{H_2O}$  to be the number of formula weights of unprotonated water molecules per litre of solution, divided by 55.5, the corresponding figure for pure water. (Thus,  $C_{H_2O}$  approaches unity at infinite dilution, in an analogous fashion to the usual convention that the activity of the solvent is unity in pure solvent.) Using these assumptions equation (6) now becomes

$$-H_o = \log C - n \log (C/m)(1 - 0.018 nm) \quad (7)$$

where  $m$  is the stoichiometric molality of the acid. The factor  $C/m$  is required to give the correct concentration units (molar). Using  $n=4$  as before, the calculated values of  $H_o$  were found to be within 0.1 logarithmic units of the observed values up to about 8 m for HCl, HBr,  $HClO_4$  and  $H_2SO_4$ .

Using the empirical relationship  $m/C = 1 + \beta m$ , where  $\beta$  is a constant characteristic of the acid under consideration, and expanding the logarithmic term in equation (7) as far as the first term gives

$$-H_o \simeq \log m + 0.434m [(n-1)\beta + 0.018n^2] \quad (8)$$

Plotting  $(H_o + \log m)$  vs  $m$  and evaluating  $n$  from the slope gives  $n=4.4$  for HCl, HBr and  $H_2SO_4$ , and  $n=4.0$  for  $HClO_4$ .

Bascombe and Bell point out that their model must fail at about 14 m, since above this concentration there is no longer sufficient water



present to form  $\text{H}_9\text{O}_4^+$ . There are no discontinuities in  $\text{H}_0$  as a function of acid concentration, indicating that the change in hydration number must be a continuous process rather than an abrupt change from  $n=4$  to, say,  $n=3$ , so this model would be expected to fail somewhat below the upper limit of 14 m. In fact, it fails above about 8 m.

#### Wyatt's Treatment of Sulfuric Acid.

At the same time that Bascombe and Bell<sup>11</sup> were considering the possibility of hydration of the oxonium ion in moderately concentrated acids, Wyatt<sup>13</sup> was attempting to determine whether or not hydration could be responsible for the behavior of concentrated sulfuric acid. In Wyatt's words, "It has often proved useful in dealing with complex solution problems to accept the hypothesis that, notwithstanding the well-established theory of physical departure from ideality, any very large changes in activity coefficients are probably capable of some chemical explanation. In concentrated acid solutions, the changes in the acidity function and water activity are much larger than would be expected from the simplest chemical picture of straightforward ionization . . . ." <sup>13</sup>

Wyatt first considered the possibility of hydration of either  $\text{HSO}_4^-$  or  $\text{H}_3\text{O}^+$  in the neighbourhood of the composition  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . The calculated (mole fraction) equilibrium constants were more nearly constant for hydration of the oxonium ion, and hence he considered this to be the more promising approach.

One of the consequences of his treatment was the prediction that







the acidity function of solutions of all completely ionized acids should be a common function of the water activity only. This does indeed seem to be the case for  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ , although he pointed out that plots of the acidity function against the activity of water would not be expected to be sensitive to moderate departures of  $\alpha$  (the degree of dissociation) from unity. For a given value of the activity of water, the difference between the acidity functions for a strong and a weak acid is given by <sup>13</sup>

$$(\text{H}_\text{O})_\text{weak} - (\text{H}_\text{O})_\text{strong} = \log \left[ (1 + \alpha)/2\alpha \right] \quad (9)$$

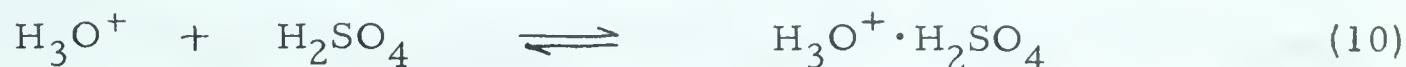
Thus, a value of  $\alpha=0.5$  would shift  $\text{H}_\text{O}$  by 0.18 units,  $\alpha=0.1$  by 0.74 units,  $\alpha=2$  (e.g. complete dissociation of  $\text{HSO}_4^-$ ) by -0.12. Hence, a range of values of  $\alpha$  from about 0.5 to 2 would cause a shift in  $\text{H}_\text{O}$  corresponding to only a few times the probable error in  $\text{H}_\text{O}$ .<sup>14</sup> Thus  $\text{H}_2\text{SO}_4$ , for which  $1 < \alpha < 2$  up to about 14M,<sup>7,15,16</sup> and  $\text{HNO}_3$ , for which  $\alpha > 0.5$  up to about 10 M,<sup>17,18</sup> both fall on the curve common to monobasic strong acids. This method should, however, provide a means of determining the degree of dissociation of weaker acids.

Bascombe and Bell<sup>11</sup> had noted that for a given value of the molality in the range  $m=1$  to 10,  $\text{H}_\text{O}$  had very nearly the same value for a number of strong acids. This is compatible with Wyatt's observation if it is assumed that the activity of water is determined mainly by the ratio of the concentration of the proton to the stoichiometric concentration of water, and that the anions either have the same effect, or more reasonably, a similar and small effect.

The major difficulty with a treatment of concentrated  $\text{H}_2\text{SO}_4$  based



on the proton species  $\text{H}^+(\text{H}_2\text{O})_2$  was found to be in the interpretation of the thermal data.<sup>13,15</sup> This was circumvented by assuming that the oxonium ion could also be solvated by  $\text{H}_2\text{SO}_4$ <sup>15</sup>, i.e.



This is in good agreement with the Raman spectral data<sup>16</sup>, which were obtained independently at nearly the same time, and which were best explained by the presence of a species  $\text{H}_5\text{SO}_5^+$ .

Wyatt<sup>13</sup> also showed that the  $\text{H}_\text{O}$  vs.  $a_{\text{H}_2\text{O}}$  curve could be represented by a power series in the activity of water. The best fit over the range 2.5 to 15 m (2.3 to 9 M  $\text{H}_2\text{SO}_4$ ) was obtained with a function corresponding to the addition of up to four molecules of water to  $\text{H}_3\text{O}^+$ , i.e. with a hydration number for the proton of up to five.

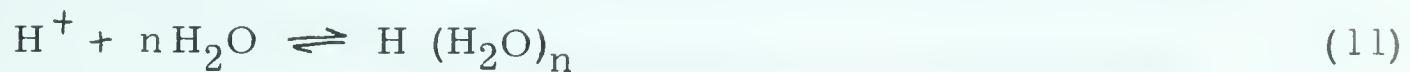
#### Høgfeldt's Treatment of Hydration in Acid Solutions.

Since 1960, Høgfeldt has published several papers dealing with the hydration of one or more of the species present in aqueous solutions of strong acids.<sup>19-22</sup> His approach has been to consider the complex equilibria between several hydrate species. The work of most interest here, the hydration of the proton, can be divided into essentially three steps:

1. the evaluation of the average hydration number of the electrolyte;<sup>19</sup>
2. the division of the total hydration number into contributions from the anion and cation;<sup>20</sup> and
3. the interpretation of the average cation (and anion) hydration numbers in terms of the individual hydrate species assumed to be present.<sup>22</sup>



Consider the reactions



where  $n$  and  $g$ , the hydration numbers of the proton and anion of a strong acid, can have any integral value. The law of mass action gives

$$C_{\text{H}^+(\text{H}_2\text{O})_n} = K_n a_{\text{H}^+} a_{\text{H}_2\text{O}}^n / f_{\text{H}^+(\text{H}_2\text{O})_n} \quad (13)$$

$$C_{\text{A}^-(\text{H}_2\text{O})_g} = K_g a_{\text{A}^-} a_{\text{H}_2\text{O}}^g / f_{\text{A}^-(\text{H}_2\text{O})_g} \quad (14)$$

where the  $C$ 's are the concentrations of the hydrate species indicated by the subscripts;  $K_n$  and  $K_g$  are true thermodynamic equilibrium constants;  $a_{\text{H}^+}$  and  $a_{\text{A}^-}$  are the activities of the unhydrated proton and anion, respectively;  $a_{\text{H}_2\text{O}}$  is the activity of water; and  $f_{\text{H}^+(\text{H}_2\text{O})_n}$  and  $f_{\text{A}^-(\text{H}_2\text{O})_g}$  are the activity coefficients of the hydrated species. The quantities which can be measured experimentally are the sums of all of the proton or anion hydrates. Hence,

$$\begin{aligned} P = \sum_n C_{\text{H}^+(\text{H}_2\text{O})_n} \\ = \frac{a_{\text{H}^+}}{f_{\text{H}^+(\text{H}_2\text{O})_n}} \sum_n K_n a_{\text{H}_2\text{O}}^n \end{aligned} \quad (15)$$

$$\begin{aligned} A = \sum_g C_{\text{A}^-(\text{H}_2\text{O})_g} \\ = \frac{a_{\text{A}^-}}{f_{\text{A}^-(\text{H}_2\text{O})_g}} \sum_g K_g a_{\text{H}_2\text{O}}^g \end{aligned} \quad (16)$$

where  $P$  and  $A$  are the total concentrations of proton and anion hydrate species





present in a solution of stoichiometric molar acid concentration  $C$ . The degree of dissociation of the acid is  $\alpha$ . Equations (15) and (16) assume that the activity coefficients of the various hydrates are the same for species differing only in the amount of water of hydration.

The average hydration number of the electrolyte can be evaluated from equations (15) and (16) by a series of mathematical manipulations (multiplication of equation (15) by equation (16), taking logarithms, and differentiating with respect to  $a_{H_2O}$ ), and the use of the equalities

$$f_{H^+} f_{A^-} = f^2 \quad (17)$$

and

$$d \log \sum_k K_i a_{H_2O}^k / d \log a_{H_2O} = \underline{k} \quad (18)$$

where  $f$  is the mean molar activity coefficient of the acid and  $\underline{k}$  is the average hydration number of the electrolyte. This procedure yields

$$\begin{aligned} \underline{k} &= \underline{n} + \underline{g} \\ &= d \log f_{H^+(H_2O)_n} f_{A^-(H_2O)_g} / d \log a_{H_2O} \\ &\quad - d \log (f/\alpha)^2 / d \log a_{H_2O} \end{aligned} \quad (19)$$

The quantities  $f_{H^+(H_2O)_n}$  and  $f_{A^-(H_2O)_g}$  cannot be evaluated at the present time. However, at high acid concentrations, Högfeldt assumed on the basis of the behavior of products of activity coefficients<sup>19</sup> that the activity coefficients of the hydrates would change fairly slowly, whereas  $a_{H_2O}$  changes rapidly so that the first term on the right hand side of equation (19) was assumed to be negligible. He then defined an approximate average hydration number,





$\underline{k}'$ , as

$$\underline{k}' = -d \log (f/\alpha)^2 / d \log a_{\text{H}_2\text{O}} \quad (20)$$

For the reason given above, and the converse argument applied to dilute acid solutions,  $\underline{k}'$  would be expected to be a fairly reliable approximation of  $\underline{k}$  in concentrated acids, i.e. for small values of  $\underline{k}$ , and a poorer approximation in dilute solution where  $\underline{k}$  is larger.

The results of applying equation (20) to  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{HNO}_3$  indicate that perchloric and sulfuric acids are more highly hydrated than nitric acid in dilute solutions. This difference seems to disappear in moderately concentrated acid. The curve for sulfuric acid (the only acid for which data was available to very high concentrations) approaches unity as the concentration increases, suggesting that the species present are  $\text{H}_3\text{O}^+$  and  $\text{HSO}_4^-$ .

In the above treatment, the difficulty of trying to evaluate the activity coefficients was circumvented by using the mean stoichiometric activity coefficient. This treatment can thus only yield the sum of  $\underline{n}$  and  $\underline{g}$ . In order to obtain these two quantities separately, it is necessary to evaluate  $f_{\text{H}^+(\text{H}_2\text{O})_n}$  and  $f_{\text{A}^-(\text{H}_2\text{O})_g}$ . This was attempted<sup>20</sup> via the Hammett acidity function, i.e.

$$h_0 = C_{\text{H}^+} f_{\text{H}^+} f_{\text{B}} / f_{\text{BH}^+} \quad (1)$$

Equation (20) can be written in the equivalent form

$$\underline{k}' = -d \log f_{\text{H}^+} f_{\text{A}^-} / d \log a_{\text{H}_2\text{O}} \quad (21)$$

and multiplication and division of  $f_{\text{H}^+} f_{\text{A}^-}$  by  $f_{\text{B}} / f_{\text{BH}^+}$  and separation of the



logarithm into two terms gives

$$\begin{aligned}\underline{k}' &= -d \log (f_{H^+} f_B / f_{BH^+}) / d \log a_{H_2O} - d \log (f_A - f_{BH^+} / f_B) / d \log a_{H_2O} \\ &= \underline{n}'' + \underline{g}''\end{aligned}\quad (22)$$

where the double primes are used to indicate that a second approximation, i.e. that  $d \log (f_B / f_{BH^+}) / d \log a_{H_2O} = 0$ , is necessary in order to split the approximate average hydration number  $\underline{k}'$  into its constituent parts. From equations (1) and (22) it can be seen that

$$\underline{n}'' = (d \log C_{H^+} + dH_o) / d \log a_{H_2O} \quad (23)$$

and from equations (20), (22) and (23) it follows that

$$\begin{aligned}\underline{g}'' &= \underline{k}' - \underline{n}'' \\ &= -d \log (f/\alpha)^2 / d \log a_{H_2O} - (d \log C_{H^+} + dH_o) / d \log a_{H_2O}\end{aligned}\quad (24)$$

For the same reason as given in the discussion of  $\underline{k}'$ , these expressions for  $\underline{n}''$  and  $\underline{g}''$  should be good approximations to the true average hydration numbers in concentrated acid solutions, and are probably less reliable in dilute solutions.

Applying equations (23) and (24) to the sulfuric acid-water system, it was found that  $\underline{n}''$  varied from about 4 in 4 M  $H_2SO_4$  to a limiting value of 1 in concentrated acid solutions. The average hydration number of the bisulfate ion,  $\underline{g}''$ , changed from about 3 to 0 over the same range.

The most recent step in Högfeldt's method was to fit the average hydration functions with individual hydrate species.<sup>22</sup> Two additional assumptions were made in order to do this:

1. it was assumed that the mathematical solution involving the fewest species

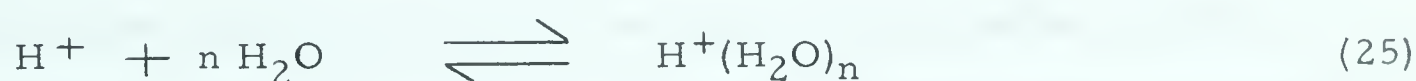


was correct; and

2. it was assumed that  $\text{H}_3\text{O}^+$  and  $\text{H}_9\text{O}_4^+$ , because of the high degree of symmetry, were more important than other hydrate species.

The same approach, which was essentially a matter of curve-fitting, was used to study both the complexes between undissociated acids and water<sup>21, 22</sup> and the ionic hydrates discussed above.<sup>22</sup> The results for the undissociated acids indicated the presence of  $\text{HNO}_3 \cdot (\text{H}_2\text{O})_3$ ,  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  and  $\text{HNO}_3$  in 0 to 24 M  $\text{HNO}_3$ ;  $\text{HClO}_4 \cdot (\text{H}_2\text{O})_7$  and  $\text{HClO}_4 \cdot (\text{H}_2\text{O})_3$  in 0 to 11 M  $\text{HClO}_4$ ; and  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  in 15 to 18.6 M  $\text{H}_2\text{SO}_4$ .

The proton hydrate species found should of course be independent of the acid; their relative abundances would depend on the concentration of dissociated acid and the activity of water and hence on the particular acid under consideration. The species used were  $\text{H}^+(\text{H}_2\text{O})_{11}$ ,  $\text{H}^+(\text{H}_2\text{O})_4$ ,  $\text{H}^+(\text{H}_2\text{O})_2$  and  $\text{H}^+(\text{H}_2\text{O})$ . The equilibrium constants for reactions of the type



were approximated by

$$\begin{aligned} K_n &= \frac{C_{\text{H}^+(\text{H}_2\text{O})_n} f_{\text{BH}^+}}{a_{\text{H}^+} a_{\text{H}_2\text{O}}^n f_{\text{B}}} \\ &= C_{\text{H}^+(\text{H}_2\text{O})_n} / h_0 a_{\text{H}_2\text{O}}^n \end{aligned} \quad (26)$$

i.e. differing from the true thermodynamic equilibrium constant by the factor  $f_{\text{BH}^+}/f_{\text{B}} f_{\text{H}^+(\text{H}_2\text{O})_n}$ . These constants were found to be the same for the systems  $\text{HNO}_3 - \text{H}_2\text{O}$  (0 to 24 M) and  $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  (0-18.6 M), but the values found for  $\text{HClO}_4 - \text{H}_2\text{O}$  (0-9 M) were not in agreement with those from the other two systems.







The average hydration curves for the anions were fitted by the species  $\text{NO}_3^-$  (0 to 14 M);  $\text{ClO}_4^- \cdot (\text{H}_2\text{O})_7$  and  $\text{ClO}_4^- \cdot \text{H}_2\text{O}$  (0 to 9 M); and  $\text{SO}_4^{2-} \cdot \text{H}^+ \cdot (\text{H}_2\text{O})_3$ ,  $\text{SO}_4^{2-} \cdot \text{H}^+ \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_4^- \cdot (\text{H}_2\text{O})_7$ ,  $\text{HSO}_4^- \cdot \text{H}_2\text{O}$  and  $\text{HSO}_4^-$  (0 to 18.6 M).

### The Present Model.

The Bascombe and Bell model<sup>11</sup> is restricted to moderately concentrated solutions because the possibility of  $n$  changing is not considered. Hence, the most obvious extension of their method is to consider a variable hydration number for the proton,  $\underline{n}$ , rather than a fixed value. Since  $\underline{n}$  will not in general be an integral number, it is necessary to consider more than one hydrate species. The present model is based on the assumption that up to four proton hydrate species can coexist in the same solution. No restrictions are placed on the values of  $\underline{n}$ , with the exception of the assumption that the free, unsolvated proton does not exist in appreciable amounts.<sup>23</sup> The calculations are done in such a way as to consider the lowest values of the hydration number consistent with the observed data.

It is assumed that there are four "types" of water present in aqueous solutions of strong acids :

1. water "clusters";<sup>24-28</sup>
2. monomeric water;<sup>24-28</sup>
3. water of proton hydration; and
4. water of anion hydration.

Hydration of the anion cannot be estimated by this approach, but the application



of Raoult's law gives some indication of its importance. Hydration of the undissociated acids is not considered, except in the case of nitric acid. The effect of hydration of the Hammett indicator and its conjugate acid is considered qualitatively.

As can be seen, the present model is similar to that of Högfeldt.<sup>19-22</sup> The similarities and differences of the two approaches will be discussed later.



## CALCULATIONS

### Proton Hydration.

If several proton hydrate species are present in a solution, the contribution of any one of them to the acidity,  $\delta_n h_o$ , will be

$$\delta_n h_o = C_{H^+(H_2O)_n} f_{H^+(H_2O)_n} f_B / a_{H_2O}^n f_{BH^+} \quad (27)$$

where  $C_{H^+(H_2O)_n}$  is the concentration of the species under consideration, the  $f$ 's are the activity coefficients of the subscripted species, and  $a_{H_2O}$  is the activity of water. The units of the activity coefficients will of course depend on the units chosen for the concentration of the proton hydrates.

The experimentally observed value of  $h_o$  is the sum of the contributions of all of the different proton hydrate species present, i.e.

$$\begin{aligned} h_o &= \sum_n \delta_n h_o \\ &= (f_B / f_{BH^+}) \sum_n (C_{H^+(H_2O)_n} f_{H^+(H_2O)_n} / a_{H_2O}^n) \end{aligned} \quad (28)$$

The stoichiometry of the system imposes two additional restrictions:

$$P = \sum_n C_{H^+(H_2O)_n} \quad (29)$$

$$\text{and} \quad Q = \sum_n n C_{H^+(H_2O)_n} \quad (30)$$

where  $P$  is the total concentration of all of the proton hydrate species and  $Q$  is the concentration of water of proton hydration. The units of  $P$  and  $Q$  must be the same, and are governed by the choice of units for the concentration of the proton hydrate species. This gives three equations involving the concentrations of proton hydrate species and hence if  $h_o$ ,  $P$ ,  $Q$  and the activity coefficients were all known, the three equations could be solved for the concentrations of three different species.

The activity coefficients are not known, so it is necessary to make





some additional assumptions about them in order to proceed with the problem. It was assumed initially that the whole factor  $f_{H^+(H_2O)_n} f_B / f_{BH^+} = 1$ . This assumption will be considered in more detail later.

Equation (28) now becomes

$$h_o = \sum_n C_{H^+(H_2O)_n} / a_{H_2O}^n \quad (31)$$

This equation and similar expressions for  $h_o$  which neglect the activity coefficients will be referred to as idealized  $h_o$  equations.

Values of  $h_o$  and  $P$ , the total concentration of proton hydrate species, are available in the literature for a number of strong acids. The evaluation of  $Q$ , the total water of proton hydration, is not so simple a matter.

There are three assumptions which could be made in order to estimate  $Q$ .

1. Assume that all of the water in the solution is involved in proton hydration.

This is probably a good approximation in very concentrated strong acid solutions, but it leads to difficulties in the dilute region, since the hydration number of the proton approaches infinity as the concentration of acid approaches zero according to this assumption.

2. Assume that the activity of water is a measure of the "free" water in solution (the water not involved in hydration of the proton) and that the solution obeys Raoult's law. In this case,

$$Q = C_{H_2O} - a_{H_2O} \sum_i C_i / (1 - a_{H_2O}) \quad (32)$$

where  $C_{H_2O}$  is the stoichiometric concentration of water and  $\sum_i C_i$  is the sum of the concentrations of all of the other species present--



proton, anion or anions, undissociated acid, etc. There are two objections to this assumption--the neglect of hydration of other species present, and the use of Raoult's law for a solution which gives no indication of being ideal.

3. Assume that the average hydration number of the proton,  $\underline{n}$ , can be obtained from the idealized  $h_o$  equation

$$h_o = P / a_{H_2O}^{\underline{n}} \quad (33)$$

in which case  $Q$  can be obtained from

$$Q = \underline{n} P \quad (34)$$

This procedure would be valid if the neglect of the activity coefficient ratio were valid, and if only one proton hydrate existed in any given solution. The difference between this  $\underline{n}$  and that obtained by other methods will be discussed later.

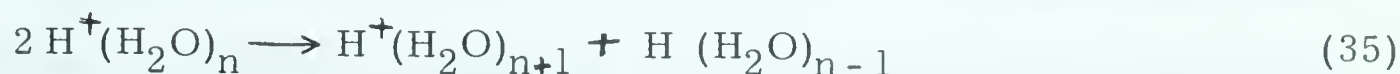
If assumptions 2 and 3 gave the same result, it would be reasonably safe to use the  $Q$  values obtained from either. However, this is not the case, and hence another approach was necessary.

The method finally used is essentially an empirical one. If an arbitrary value of  $Q$  is chosen, equations (29), (30) and (31) will yield values for the concentrations of three hydrate species, but these values will not necessarily have any physical meaning. Three criteria were used successively to determine acceptable values of  $Q$ .

1. The concentrations of all proton hydrate species must be zero or positive.
2. The concentration of the intermediary proton hydrate species cannot be less than the concentrations of both of the other two species. This is



based on the fact that in sulfuric acid, no hydrate is observed to disproportionate to a more and a less hydrated species,<sup>29</sup> i.e. the reaction



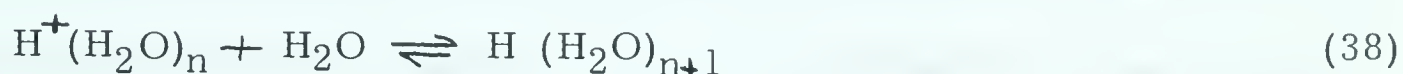
does not occur.

3. The pseudo-constants for the equilibria



$$K_n = \frac{C_{\text{H}^+(\text{H}_2\text{O})_n} C_{\text{A}^-}}{a_{\text{H}_2\text{O}}^n C_{\text{HA}}} \quad (37)$$

must be in the order  $K_{n+1} > K_n > K_{n-1}$ , etc. In other words, the reaction



$$K = \frac{C_{\text{H}^+(\text{H}_2\text{O})_{n+1}}}{C_{\text{H}^+(\text{H}_2\text{O})_n} a_{\text{H}_2\text{O}}} \quad (39)$$

has a negative free energy -- i.e. the proton tends to hydrate.

An iteration procedure was programmed for the IBM 1620 operated by the University of Alberta Computing Centre, and acceptable values of  $Q$  were obtained as a function of the stoichiometric acid concentration. Starting in concentrated acid, the species  $\text{H}_3\text{O}^+$ ,  $\text{H}^+(\text{H}_2\text{O})_2$  and  $\text{H}^+(\text{H}_2\text{O})_3$  were considered; when the concentration was reached at which no value of  $Q$  would work for these three species,  $\text{H}^+(\text{H}_2\text{O})_2$ ,  $\text{H}^+(\text{H}_2\text{O})_3$  and  $\text{H}^+(\text{H}_2\text{O})_4$  were used and so on. Species up to  $\text{H}^+(\text{H}_2\text{O})_{11}$  were considered. Preliminary results indicated that the ten species corresponding to  $n = 1, 2, \dots, 10$  were sufficient.

A range of values of  $Q$  was obtained for each concentration of acid. These results were then plotted on a large scale graph, and the values used in subsequent work were then read from a smooth curve through the "experimental points".







Once definite values of  $Q$  are obtained, equations (29), (30) and (31) can be solved simultaneously for the concentrations of three proton hydrate species. This procedure works well in concentrated solutions, but large discontinuities in the plots of  $C_{H^+(H_2O)_n}$  vs. the stoichiometric acid concentration were observed in more dilute solutions. The discontinuities correspond to the change from the program considering  $H^+(H_2O)_n$ ,  $H^+(H_2O)_{n+1}$  and  $H^+(H_2O)_{n+2}$  to the program involving  $H^+(H_2O)_{n+1}$ ,  $H^+(H_2O)_{n+2}$  and  $H^+(H_2O)_{n+3}$ . In order to reduce these discontinuities, an iteration procedure similar to that described above for  $Q$  was used. The same criteria of acceptability were used: in fact, the program was identical except that the concentration of the least hydrated proton species was now considered to be the variable. This, of course, yielded ranges of acceptable values of the concentrations of the various species and the pseudo-equilibrium constants for their formation. The procedure considerably reduced, but did not completely eliminate, the discontinuities, suggesting that at least five species coexist over a limited range. It is difficult to see how three equations can be used to yield any meaningful information about five species.

The computer calculations were carried out only for sulfuric acid, the monobasic acids being investigated only by a study of the average hydration numbers obtained from the three assumptions which could be used to obtain  $Q$ .

#### Sources of Experimental Data.

Four types of data as a function of acid concentration are required in order to apply the present model. They are density data for the conversion of concentration scales, activity of water data, acidity function data, and



information about the concentrations of the analytical species present -- proton, anion or anions, plus any other species which might not be expected from the assumption of straightforward dissociation.

The choice of units for use in the idealized  $h_0$  equations is a questionable matter. Molal units were used throughout since they gave slightly lower values of the average hydration number. However, all of the plots are on a molar basis, since the molal scale gives undue emphasis to the highly concentrated region.

Calculations were done for  $H_2SO_4$ ,  $HClO_4$ ,  $HBr$ ,  $HCl$  and  $HNO_3$ . There is not sufficient data available for a study of  $H_3PO_4$ . The sources of data, as well as a brief description of any special problems, are given below for each of the five acids studied.

The data used directly in the calculations are summarized in Tables 1 to 5, and densities, concentration conversion factors and other data used indirectly are tabulated in the Appendix. All data refer to  $25^\circ C$ .

#### Sulfuric Acid.

Sulfuric acid has the disadvantage of being dibasic, which complicates the calculations in that both anions must be considered. To make up for this, it has two very important advantages: it seems to be the most thoroughly studied of the strong acids, there being an abundance of good data available, and it is the only common strong acid which can be conveniently studied over the entire range from pure water to pure acid. Calculations were done on  $H_2SO_4$  over the range 0.1 to 1000 m (1 - 99% by weight). This seems to avoid complications caused by reactions such as







which are important at very high acid concentrations. Below 0.1 m, the activity of water is so nearly equal to unity that more than the eight significant figures normally carried by the computer are required to give finite answers.

Density data were taken from the International Critical Tables.<sup>30</sup> The values at rounded molalities were obtained by numerical interpolation of the tabulated data. Values of the activity of water were taken from the recent work of Giauque, et al.<sup>29</sup> at concentrations of 1m and greater, and from the EMF data of Harned and Hamer<sup>31</sup> at concentrations below 1 m. For concentrations not listed in either of these papers, values were estimated graphically from large scale plots of the data. Values of the acidity function were obtained graphically from large scale plots of the results of Bascombe and Bell in dilute solution<sup>32</sup>, the revised values reviewed by Paul and Long in the intermediate region<sup>14</sup>, and the recent redetermination of Jorgensen and Hartter in concentrated solutions.<sup>33</sup> The concentrations of analytical species were taken from the Raman work of Young and co-workers — from the table in reference (7) for concentrations below 35 m, and from the graph in reference (16) for concentrations above 35 m. It should be noted in this connection that allowance was made for  $\text{H}_5\text{SO}_5^+$ <sup>15,16</sup> --- it was assumed that its contribution to  $h_0$  was the same as the same concentration of  $\text{H}_3\text{O}^+$  would have been. This is not important, however, since although the concentration of  $\text{H}_3\text{O}^+$  is relatively large in the region in which  $\text{H}_5\text{SO}_5^+$  exists, the activity of water is so low that the more highly hydrated species are far more important in determining the acidity.





TABLE 1. DATA FOR SULFURIC ACID(b).

Conc. of $\text{H}_2\text{SO}_4$	$^a\text{H}_2\text{O}$	$h_o$	P	Q	$\text{C}_{\text{SO}_4^{2-}}$	$\text{C}_{\text{HSO}_4^-}$	$\text{C}_{\text{H}_2\text{SO}_4}$	$\text{C}_{\text{H}_5\text{SO}_5^+}$
$m\text{H}_2\text{SO}_4$	$\text{C}_{\text{H}_2\text{SO}_4}$							
0.1	0.9964	0.136	0.132	0.579	0.033	0.066		
0.2	0.9928	0.275	0.260	1.38	0.062	0.136		
0.3	0.9892	0.418	0.383	2.24	0.087	0.210		
0.4	0.9857	0.572	0.508	3.26	0.114	0.279		
0.5	0.9821	0.735	0.631	4.40	0.141	0.349		
0.6	0.9784	0.907	0.754	5.68	0.168	0.418		
0.7	0.9746	1.09	0.874	7.03	0.193	0.488		
0.8	0.9706	1.28	0.992	8.46	0.217	0.558		
0.9	0.9664	1.51	1.11	9.92	0.24	0.62		
1.0	0.9621	1.77	1.24	11.49	0.28	0.68		
1.5	0.9402	3.43	1.82	18.12	0.40	1.01		
2.0	0.9130	6.28	2.46	24.24	0.60	1.25		
2.5	0.8833	10.6	3.01	28.78	0.73	1.55		
3.0	0.8514	17.5	3.58	33.02	0.90	1.78		
3.5	0.8169	27.1	4.08	35.76	1.01	2.06		
4.0	0.7800	40.6	4.59	37.37	1.14	2.31		
4.5	0.7421	59.8	5.06	38.88	1.25	2.56		
5	0.7035	87.0	5.52	39.40	1.36	2.79		
6	0.6257	152	6.35	40.09	1.54	3.27		
7	0.5503	301	7.10	40.18	1.69	3.73		
8	0.4806	565	7.76	39.57	1.78	4.20		
9	0.4175	$1.08 \times 10^3$	8.34	38.70	1.84	4.67		
10	0.3611	$2.08 \times 10^3$	8.86	37.74	1.86	5.14		
11	0.3113	$3.71 \times 10^3$	9.31	36.77	1.85	5.61		
12	0.2678	$6.38 \times 10^3$	9.71	35.80	1.82	6.08		
13	0.2303	$1.04 \times 10^4$	10.06	34.84	1.77	6.53		
14	0.1980	$1.64 \times 10^4$	10.38	33.91	1.70	6.98		
15	0.1701	$2.54 \times 10^4$	10.66	33.02	1.62	7.41		



TABLE 1. - Continued

Conc. of H <sub>2</sub> SO <sub>4</sub> mH <sub>2</sub> SO <sub>4</sub>	$\frac{C_{H_2SO_4}}{C_{H_2SO_4}}$	<sup>a</sup> H <sub>2</sub> O	h <sub>o</sub>	P	Q	C <sub>SO<sub>4</sub><sup>=</sup></sub>	C <sub>HSO<sub>4</sub><sup>-</sup></sub>	C <sub>H<sub>2</sub>SO<sub>4</sub></sub>	C <sub>H<sub>5</sub>SO<sub>5</sub><sup>+</sup></sub>
16	9.376	1.462 x 10 <sup>-1</sup>	3.84 x 10 <sup>4</sup>	10.91	32.16	1.54	7.84		
17	9.696	1.255 x 10 <sup>-1</sup>	5.81 x 10 <sup>4</sup>	11.14	31.34	1.45	8.25		
18	9.998	1.077 x 10 <sup>-1</sup>	8.49 x 10 <sup>4</sup>	11.35	30.55	1.36	8.64		
19	10.28	9.233 x 10 <sup>-2</sup>	1.21 x 10 <sup>5</sup>	11.55	29.79	1.27	9.02		
20	10.55	7.929 x 10 <sup>-2</sup>	1.73 x 10 <sup>5</sup>	11.73	29.06	1.18	9.38		
22	11.06	5.906 x 10 <sup>-2</sup>	3.52 x 10 <sup>5</sup>	12.08	27.70	1.03	10.03		
25	11.72	3.799 x 10 <sup>-2</sup>	8.77 x 10 <sup>5</sup>	12.55	25.87	0.84	10.88		
30	12.63	1.937 x 10 <sup>-2</sup>	3.13 x 10 <sup>6</sup>	13.24	23.27	0.61	12.02	0.00	
35	13.37	1.042 x 10 <sup>-2</sup>	8.59 x 10 <sup>6</sup>	13.58	21.12	0.41	12.77	0.19	0.00
40	13.96	5.09 x 10 <sup>-3</sup>	1.94 x 10 <sup>7</sup>	13.64	19.32	0.27	13.10	0.59	0.006
45	14.45	3.53 x 10 <sup>-3</sup>	3.87 x 10 <sup>7</sup>	13.24	17.78	0.16	12.93	1.36	0.01
50	14.86	2.23 x 10 <sup>-3</sup>	6.79 x 10 <sup>7</sup>	12.73	16.47	0.08	12.57	2.19	0.02
60	15.49	1.05 x 10 <sup>-3</sup>	1.62 x 10 <sup>8</sup>	11.63	14.32	0.02	11.59	3.82	0.05
70	15.95	5.80 x 10 <sup>-4</sup>	3.16 x 10 <sup>8</sup>	10.75	12.64	0.005	10.74	5.10	0.10
80	16.29	3.61 x 10 <sup>-4</sup>	5.27 x 10 <sup>8</sup>	10.05	11.30	0.00	10.05	6.08	0.16
90	16.56	2.47 x 10 <sup>-4</sup>	7.87 x 10 <sup>8</sup>	9.40	10.21		9.40	6.94	0.22
100	16.77	1.79 x 10 <sup>-4</sup>	1.14 x 10 <sup>8</sup>	8.79	9.31		8.79	7.69	0.29
150	17.42	6.27 x 10 <sup>-5</sup>	3.94 x 10 <sup>9</sup>	6.34	6.45		6.34	10.45	0.63
200	17.74	3.20 x 10 <sup>-5</sup>	7.53 x 10 <sup>10</sup>	4.89	4.92		4.89	11.91	0.94
300	18.05	1.38 x 10 <sup>-5</sup>	1.47 x 10 <sup>10</sup>	3.34	3.34		3.34	13.37	1.34
400	18.21	7.87 x 10 <sup>-6</sup>	2.06 x 10 <sup>10</sup>	2.52	2.53		2.52	14.04	1.64
500	18.30	5.20 x 10 <sup>-6</sup>	2.57 x 10 <sup>10</sup>	2.03	2.03		2.03	14.42	1.85
1000	18.46	1.50 x 10 <sup>-6</sup>	4.90 x 10 <sup>10</sup>	1.02	1.02		1.02	16.44	1.00

For definition of symbols and sources of data, see text. All concentrations except column 1 are in molar units.



### Perchloric Acid.

From a theoretical point of view, perchloric acid is probably the acid of choice for studies of concentrated solutions of strong acids since it is one of the strongest acids known,<sup>34,35</sup> it is monobasic and it exists in concentrations up to 100%  $\text{HClO}_4$ . From the experimental point of view, the picture is not so bright. The high oxidizing power of the concentrated acid<sup>35</sup> makes it difficult to work with, and a maximum in the melting point diagram shows that the monohydrate melts at about  $50^\circ\text{C}$ .<sup>35</sup> In addition, the pure acid is unstable to heat.<sup>35</sup> It is nonetheless unfortunate that more extensive data is not available in the more dilute region.

Density data for  $\text{HClO}_4$  are from Markham<sup>36</sup> up to 65%, and from the Handbook of Chemistry and Physics<sup>37</sup> for 65 to 75% acid. The values used were obtained by numerical interpolation of the tabulated data. The activity of water was taken mainly from Robinson and Baker<sup>38</sup>, with less weight being given to the results of Pearce and Nelson.<sup>39</sup> Acidity function data in dilute solutions were obtained in connection with the present study.<sup>40</sup> At higher acid concentrations, the new data are in agreement with the previous values.<sup>14</sup>

It was assumed that the dissociation of perchloric acid is complete up to the concentration corresponding to the monohydrate. This is not the interpretation which is put on the existing NMR data<sup>17,18</sup>, but apparently the NMR results do not agree with the unpublished Raman data<sup>18</sup>. There are two reasons for the assumption of complete dissociation. First, perchloric acid is at least as strong an acid as  $\text{H}_2\text{SO}_4$ <sup>34,35</sup> and the reaction

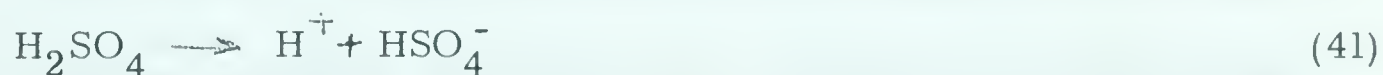




TABLE 2. DATA FOR PERCHLORIC ACID<sup>(c)</sup>.

<u>Conc. of HClO<sub>4</sub></u>		<sup>a</sup> H <sub>2</sub> O	-H <sub>2</sub> O	C <sub>H<sub>2</sub>O</sub>
m <sub>HClO<sub>4</sub></sub>	C <sub>HClO<sub>4</sub></sub>			
0.1	0.993	0.99658	-0.947	55.10
0.2	0.1976	0.99317	-0.618	54.86
0.3	0.2949	0.98968	-0.414	54.56
0.4	0.3918	0.98618	-0.245	54.38
0.5	0.4877	0.98258	-0.114	54.14
0.6	0.5827	0.97883	-0.011	53.91
0.7	0.6769	0.97517	0.070	53.67
0.8	0.7702	0.97150	0.138	53.44
0.9	0.8628	0.96734	0.203	53.21
1.0	0.9546	0.96319	0.262	52.99
1.5	1.402	0.9399	0.511	51.89
2.0	1.832	0.9165	0.704	50.84
2.5	2.245	0.8875	0.892	49.84
3.0	2.654	0.8585	1.073	48.88
3.5	3.024	0.8250	1.249	47.96
4.0	3.393	0.7915	1.420	47.08
4.5	3.749	0.7538	1.594	46.24
5.0	4.092	0.7158	1.767	45.43
6	4.745	0.6343	2.098	43.90
7	5.360	0.5512	2.441	42.50
8	5.934	0.4687	2.793	41.18
9	6.479	0.3962	3.200	39.96
10	6.988	0.3195	3.589	39.14
11	7.474	0.2558	3.940	37.72
12	7.928	0.2030	4.269	36.67
13	8.361	0.1563	4.585	35.70
14	8.768	0.1223	4.883	34.76
15	9.150	0.0939	5.164	33.86
16	9.513	0.0702	5.431	33.00

c For definitions of symbols and sources of data, see text.



which neglects hydration, goes to completion up to about 12 or 14 M<sup>7, 16, 41</sup>

which is about 35m, so HClO<sub>4</sub> would be expected to be completely dissociated



up to the highest concentration studied here — 9.5M or 16 m. Secondly, it has been shown by both NMR<sup>42,43</sup> and X-ray diffraction<sup>44</sup> studies that the solid monohydrate exists in the form  $\text{H}_3\text{O}^+ \text{ClO}_4^-$  — i.e. completely dissociated. It therefore seems reasonable that the acid would be completely dissociated at lower acid concentrations where the ratio of the concentration of water to the concentration of acid is more favorable for complete dissociation, although the change of phase makes the comparison risky. In any case, complete dissociation seems more reasonable than the use of the NMR results<sup>17,18</sup> which give  $K_A = 38$  for  $\text{HClO}_4$ , compared to 22 for nitric acid.

#### Hydrobromic Acid.

Hydrobromic acid is one of the less studied of the strong acids, but it is very nearly as satisfactory as  $\text{HClO}_4$  for a study such as the present one. It is a considerably stronger acid than  $\text{HCl}$ , and not a great deal weaker than  $\text{HClO}_4$ <sup>34</sup>. Thus it would be expected to be very nearly completely dissociated at concentrations up to 10M, the range for which data is available. It shares with  $\text{HCl}$  the disadvantage of the pure acid being a gas at room temperature.

Density data for  $\text{HBr}$  are available in the International Critical Tables<sup>30</sup>. The values used were interpolated from the tabulated data. The activity of water in  $\text{HBr}$  solutions, as well as  $\text{HCl}$  and  $\text{HI}$ , has recently been published<sup>45</sup>. The acidity function data from Paul and Long's review was used<sup>14</sup>; the values at rounded molalities were obtained by graphical interpolation of large scale plots.



TABLE 3. DATA FOR HYDROBROMIC ACID<sup>(d)</sup>.

<u>Conc. of HBr</u>		$a_{\text{H}_2\text{O}}$	$-\text{H}_\text{O}$	P	$\text{C}_{\text{H}_2\text{O}}$
$m_{\text{HBr}}$	$\text{C}_{\text{HBr}}$				
0.1	0.0995	0.9968	-0.995	0.0995	55.21
0.2	0.1984	0.9934	-0.674	0.1984	55.07
0.3	0.2969	0.9900	-0.481	0.2969	54.94
0.4	0.3949	0.9862	-0.334	0.3949	54.81
0.5	0.4924	0.9824	-0.209	0.4924	54.67
0.6	0.5894	0.9784	-0.116	0.5894	54.53
0.7	0.6860	0.9742	-0.030	0.6860	54.40
0.8	0.7820	0.9702	0.047	0.7820	54.26
0.9	0.8776	0.9660	0.116	0.8776	54.13
1.0	0.9726	0.9618	0.186	0.9726	53.99
1.5	1.441	0.9392	0.444	1.441	53.33
2.0	1.898	0.9130	0.661	1.898	52.68
2.5	2.343	0.8842	0.845	2.343	52.03
3.0	2.780	0.8532	1.018	2.780	51.44
3.5	3.205	0.8196	1.186	3.205	50.83
4.0	3.620	0.7834	1.352	3.620	50.24
4.5	4.026	0.7452	1.516	4.026	49.66
5.0	4.423	0.7050	1.687	4.423	49.10
6	5.193	0.6206	2.019	5.193	48.04
7	5.927	0.5362	2.348	5.925	47.00
8	6.629	0.4558	2.677	6.617	45.99
9	7.302	0.3826	2.998	7.217	45.04
10	7.942	0.3177	3.314	7.760	44.08
11	8.559	0.2620	3.648	8.288	43.19
12	9.145	0.2149	3.971	8.781	42.30
13	9.708	0.1757	4.282	9.258	41.45
14	10.247	0.1435	4.579	9.716	40.63

d For definition of symbols and sources of data, see text. P is in molar units.

The only approach available for the estimation of the degree of dissociation of HBr at present is that suggested by Hogfeldt.<sup>46</sup> Writing equation (1) in logarithmic form,

$$-\text{H}_\text{O} = \log \text{C}_{\text{H}^+} + \log (f_{\text{H}^+} f_{\text{B}} / f_{\text{BH}^+}) \quad (42)$$





where  $C_{H^+}$  is the molar concentration of proton, and the  $f$ 's are the molar activity coefficients of the subscripted species, Høgfelt postulates that the activity coefficient term is the same for all the strong acids at the same value of  $H_O$  and hence by plotting  $\log (f_{H^+} f_B / f_{BH^+})$  vs.  $H_O$  for an acid for which  $C_{H^+}$  is known,  $C_{H^+}$  can be obtained for a second acid. A plot of this type is shown in figure 1. The curves for  $HClO_4$  and  $H_2SO_4$  are obtained from the data given above; using  $HClO_4$  as a reference gave values of  $\alpha$ , the degree of dissociation, which seem to approach about 0.9 at infinite dilution, while the use of  $H_2SO_4$  as a reference gave values of  $\alpha$  which approach about 1.1 in very dilute solution. The curve for  $HBr$  corresponds to an average of the two results and gave an  $\alpha$  of unity at infinite dilution. The values of  $\alpha$  obtained in this way are listed in the Appendix.

#### Hydrochloric Acid.

Hydrochloric acid is weaker than any of the three acids considered above, and consequently lacks the advantage of very nearly complete dissociation. It also lacks the practical advantage of  $H_2SO_4$  of being available experimentally at all concentrations up to 100% acid. It is, however, one of the more commonly used acids, and hence it is of interest to investigate its behavior.

Density data from the International Critical Tables were used<sup>30</sup>, again using numerical interpolation to obtain the values for rounded molalities. The activity of water was taken from Randall and Young<sup>47</sup> at concentrations of 16m and less, and from Landolt-Börnstein<sup>48</sup> for 17 and 18 m. These values



Figure 1. Høgfeldt plot of the logarithm of the activity coefficient ratio vs.  $H_o$  for  $H_2SO_4$ ,  $HClO_4$  and  $HNO_3$ .



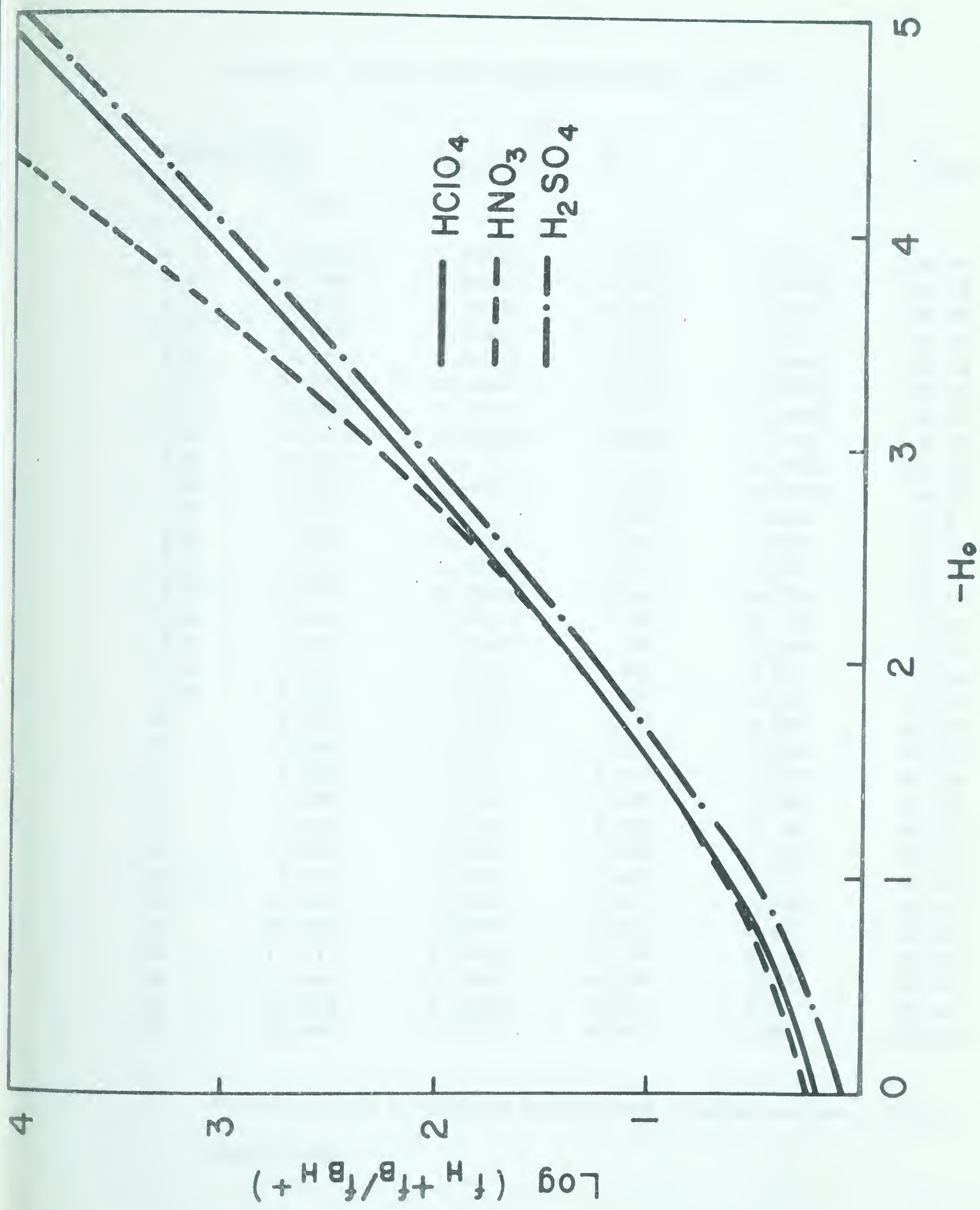






TABLE 4. DATA FOR HYDROCHLORIC ACID<sup>(e)</sup>.

<u>Conc. of HCl</u>		$a_{\text{H}_2\text{O}}$	$-\text{H}_\text{O}$	P	$\text{C}_{\text{H}_2\text{O}}$
$m_{\text{HCl}}$	$\text{C}_{\text{HCl}}$				
0.1	0.0995	0.99660	-0.992	0.0995	55.24
0.2	0.1987	0.99321	-0.677	0.1985	55.14
0.3	0.2975	0.98975	-0.480	0.2970	55.04
0.4	0.3959	0.98623	-0.339	0.3951	54.94
0.5	0.4940	0.98262	-0.218	0.4928	54.84
0.6	0.5916	0.97891	-0.114	0.5899	54.73
0.7	0.6889	0.97509	-0.025	0.6866	54.63
0.8	0.7858	0.97124	0.048	0.7827	54.53
0.9	0.8824	0.96726	0.118	0.8786	54.42
1.0	0.9787	0.96324	0.180	0.9740	54.32
1.5	1.454	0.94141	0.447	1.435	53.81
2.0	1.920	0.91750	0.646	1.878	53.30
2.5	2.378	0.89224	0.822	2.306	52.79
3.0	2.826	0.86452	0.984	2.718	52.29
3.5	3.266	0.83515	1.140	3.115	51.80
4.0	3.698	0.80401	1.299	3.498	51.31
4.5	4.121	0.77189	1.447	3.867	50.84
5.0	4.536	0.73890	1.596	4.222	50.36
6	5.343	0.67106	1.874	4.895	49.43
7	6.120	0.6027	2.162	5.520	48.53
8	6.868	0.5361	2.448	6.102	47.66
9	7.588	0.4720	2.703	6.642	46.80
10	8.281	0.4146	2.965	7.145	45.97
11	8.947	0.3623	3.190	7.612	45.15
12	9.597	0.3162	3.436	8.051	44.39
13	10.205	0.2739	3.672	8.449	43.57
14	10.799	0.2371	3.913	8.824	42.82
15	11.371	0.2002	4.150	9.174	42.08
16	11.922	0.1740	4.374	9.499	41.36
17	12.452	0.1496	4.591	9.801	40.66
18	12.980	0.1279	4.812	10.093	40.03

e For definitions of symbols and sources of data, see text. P is in molar units.



are in good agreement with more recent work of Haase, Naas and Thumm<sup>45</sup>. The acidity function for HCl was estimated from a large scale plot of the data given in Paul and Long<sup>14</sup>, with some weight being given to Milyaeva's values<sup>49</sup>. The latter data were corrected to Paul and Long's "best"  $pK_A$  values for the indicators, and the concentrations of acid were corrected to 25°C since the data were obtained at 17°C.

The degree of dissociation,  $\alpha$ , was evaluated from the Høgfeldt plot<sup>46</sup> in the same manner as discussed for HBr. It was found that the curve for HBr gave the most reasonable values. Use of the values of  $C_{H^+}$  read from the plot gave a considerable amount of scatter in the curve of  $\alpha$  vs. concentration of HCl, although the  $C_{H^+}$  vs.  $C_{HCl}$  curve appeared quite smooth. It was found that the equation

$$C_{H^+} = 1.0130C_{HCl} - 0.018140C_{HCl}^2 \quad (43)$$

fit the data within the accuracy of reading the points from the graph, and values of  $C_{H^+}$  calculated from this equation were used in determining  $\alpha$ .

#### Nitric Acid.

Nitric acid is a considerably weaker acid than any of the others considered here<sup>34</sup>, and is of interest for this reason if for no other. It shares with  $H_2SO_4$  the advantage of being stable over the entire range of concentrations, and there is a considerable body of data pertaining to its behavior. It is thought that various hydrates of the undissociated acid are present, and probably some polymers at higher acid concentration, but there do not seem to be enough data available at present for a quantitative interpretation of these



effects<sup>21</sup>.

Densities were interpolated numerically from the data given in the International Critical Tables<sup>30</sup>. There is a considerable amount of scatter in the experimental data on the activity of water in these solutions. This data has recently been reviewed by Høgfeldt<sup>21,50</sup>, and smoothed values from the tables given by him were used at concentrations above 1 m. The osmotic coefficient data given by Robinson and Stokes<sup>51</sup> were used up to 3 m, the region between 1 and 3 m being used to smooth the one set of data into the other.

The acidity function at rounded molalities was estimated graphically from large scale plots of the data from Paul and Long<sup>14</sup>, Dawber and Wyatt<sup>52</sup> and Milyaeva<sup>49</sup>, more weight being given to the first two. The data of Milyaeva were corrected to the "best"  $pK_A$ 's of the indicators and for the change of concentration with temperature, as with HCl. Dawber and Wyatt's data at concentrations above 16 M  $HNO_3$  are based on a comparison with  $H_2SO_4$ ; these were corrected to the more recent works of Jorgensen and Hartter<sup>33</sup>, and the concentrations were corrected to 25°C since the data refer to 20°C.

In the case of  $HNO_3$ , the Raman<sup>7</sup> and NMR<sup>17,18</sup> results are in agreement, and since the Raman results have apparently not been published in detail, the NMR results were used. They were completely recalculated using the experimental data in reference (18) and the far more reliable diamagnetic susceptibilities recently published<sup>53</sup>. This treatment leads to





TABLE 5. DATA FOR NITRIC ACID<sup>(f)</sup>.

$m_{\text{HNO}_3}$	$\frac{\text{Conc. of HNO}_3}{C_{\text{HNO}_3}}$	$^a\text{H}_2\text{O}$	$-\text{H}_2\text{O}$	P	$C_{\text{H}_2\text{O}}$
0.1	0.0994	0.99660	-0.936	0.0990	55.18
0.2	0.1982	0.99327	-0.578	0.1968	55.02
0.3	0.2965	0.98994	-0.370	0.2932	54.86
0.4	0.3942	0.98655	-0.205	0.3884	54.70
0.5	0.4913	0.98315	-0.080	0.4822	54.54
0.6	0.5878	0.97967	0.011	0.5747	54.38
0.7	0.6837	0.97616	0.093	0.6661	54.22
0.8	0.7791	0.97260	0.162	0.7560	54.06
0.9	0.8739	0.96912	0.222	0.8449	53.90
1.0	0.9682	0.96534	0.275	0.9326	53.74
1.5	1.431	0.94650	0.518	1.352	52.97
2.0	1.881	0.92646	0.718	1.743	52.21
2.5	2.318	0.9065	0.878	2.105	51.48
3.0	2.743	0.889	1.018	2.440	50.76
3.5	3.156	0.871	1.161	2.749	50.05
4.0	3.556	0.851	1.290	3.033	49.35
4.5	3.945	0.834	1.404	3.297	48.67
5	4.323	0.813	1.503	3.534	48.00
6	5.048	0.776	1.691	3.955	46.70
7	5.733	0.736	1.847	4.299	45.46
8	6.381	0.698	1.993	4.574	44.28
9	6.992	0.661	2.126	4.790	43.12
10	7.565	0.624	2.264	4.948	41.99
11	8.106	0.589	2.372	5.059	40.90
12	8.616	0.557	2.482	5.127	39.86
13	9.100	0.527	2.586	5.163	38.86
14	9.558	0.497	2.683	5.171	37.90
15	9.992	0.469	2.776	5.117	36.98
16	10.401	0.442	2.861	5.108	36.08
17	10.788	0.417	2.949	5.049	35.23
18	11.154	0.394	3.037	4.970	34.40
19	11.503	0.372	3.113	4.881	33.60
20	11.833	0.351	3.190	4.779	32.84
22	12.446	0.313	3.334	4.555	31.40
25	13.260	0.264	3.529	4.169	29.44
30	14.384	0.204	3.807	3.491	26.62
35	15.297	0.159	4.019	2.891	24.26
40	16.050	0.126	4.202	2.465	22.27
45	16.681	0.101	4.350	2.142	20.58
50	17.218	0.0838	4.479	1.894	19.11



TABLE 5. - Continued

<u>Conc. of HNO<sub>3</sub></u>		$a_{\text{H}_2\text{O}}$	$-H_{\text{O}}$	P	$C_{\text{H}_2\text{O}}$
$m_{\text{HNO}_3}$	$C_{\text{HNO}_3}$				
60	18.081	0.0594	4.688	1.484	16.73
70	18.747	0.0438	4.861	1.187	14.87
80	19.273	0.0335	4.995	0.954	13.37
90	19.701	0.0264	5.112	0.776	12.15
100	20.052	0.0215	5.210	0.658	11.13
150	21.171	0.00975	5.545	0.320	7.834
200	21.762	0.00585	5.728	0.192	6.040
300	22.376	0.00312	5.916	0.087	4.140
400	22.699	0.00209	6.020	0.054	3.150
500	22.899	0.00158	6.073	0.044	2.542
1000	23.342	0.000743	6.208	0.021	1.296

f For definitions of symbols and sources of data, see text. P is in molar units.

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negative values of  $\alpha$  above 20 M, and hence above 16 M, values were estimated from the graph in reference 7.

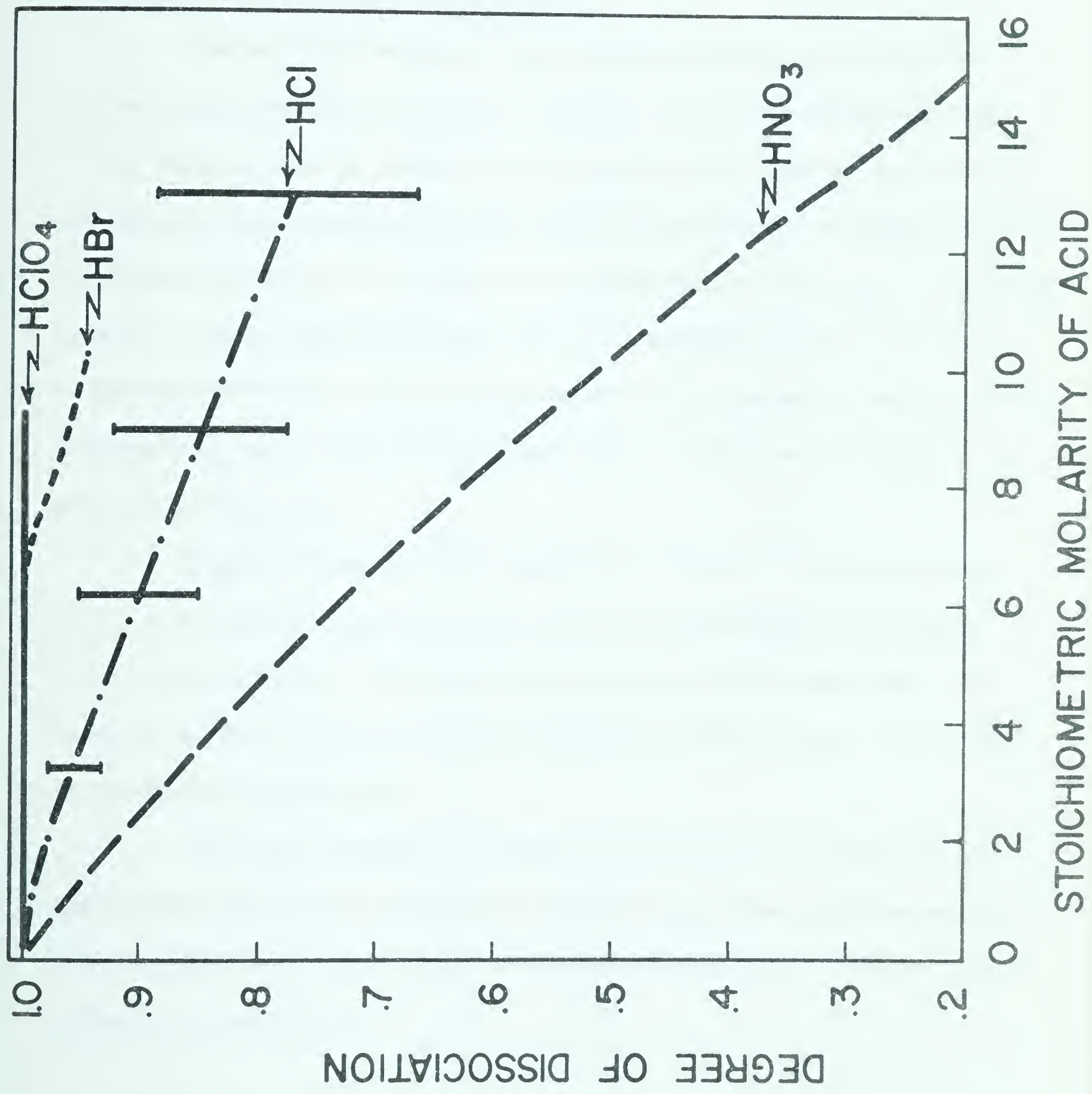
Figure 2 shows  $\alpha$  as a function of the stoichiometric acid concentration for the four monobasic acids considered. The vertical bars drawn in along the curve for HCl correspond to an error of 50% in the concentration of the undissociated acid. The effect of error in these methods will be discussed later.



Figure 2. The degree of dissociation,  $\alpha$ , as a function of the stoichiometric concentration of acid for  $\text{HClO}_4$ ,  $\text{HBr}$ ,  $\text{HCl}$  and  $\text{HNO}_3$ .









## RESULTS

### Average Hydration Number of the Proton.

Values of the average proton hydration number,  $\underline{n}$ , for each of the five acids considered are listed in Tables 6 to 10. The column headings are as follows:  $m$  is the stoichiometric molarity of the acid;  $\underline{n}_S$  is the average hydration number assuming all of the water in the solution is hydrating the proton according to assumption (1) (Calculations section);  $\underline{n}_R$  is the average hydration number assuming Raoult's law as in assumption (2);  $\underline{n}_H$  is the average hydration number derived from the idealized  $h_O$  equation, assumption (3); and finally  $\underline{n}_C$  is the range of acceptable values found from the computer program for sulfuric acid.

Figure 3 illustrates the data given in Table 6. The curve shown for  $\underline{n}_C$  was drawn through the vertical lines corresponding to the range of values given in Table 6, and represents the values used in later work. The values of  $Q$ , the total water of proton hydration, listed in Table 1 are related to this line by equation (34).

The general shapes of the plots for perchloric, hydrobromic and hydrochloric acids are very similar, except for  $\underline{n}_H$  in the region below about 2 M. Figure 4 shows the average proton hydration numbers from the three assumptions for  $\text{HClO}_4$ .



TABLE 6. AVERAGE HYDRATION NUMBER OF THE PROTON  
SULFURIC ACID

m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$	$\bar{n}_C$
0.1	416.	-62.	4.49	4.371 - 4.372
0.2	212.	-32.	5.22	5.326 - 5.327
0.3	143.	-19.	5.88	5.865 - 5.865
0.4	108.	-15.	6.48	6.411 - 6.413
0.5	86.2	-12.	7.00	6.975 - 6.975
0.6	71.9	- 8.6	7.52	7.531 - 7.534
0.7	61.8	- 6.3	8.04	8.045 - 8.045
0.8	54.2	- 4.8	8.52	8.526 - 8.530
0.9	48.1	- 3.2	8.93	8.908 - 8.908
1.0	43.0	- 2.1	9.24	9.243 - 9.245
1.5	28.8	.8	9.95	9.948 - 9.949
2.0	21.0	2.6	9.89	9.867 - 9.871
2.5	16.8	3.53	9.61	9.560 - 9.577
3.0	13.8	3.82	9.26	9.212 - 9.227
3.5	11.9	4.12	8.79	8.754 - 8.769
4.0	10.4	4.23	8.21	8.126 - 8.146
4.5	9.28	4.25	7.74	7.681 - 7.708
5.	8.36	4.20	7.24	7.121 - 7.154
6.	7.01	4.08	6.42	6.274 - 6.357
7.	6.05	3.89	5.84	5.651 - 5.798
8.	5.35	3.71	5.46	>5.234
9.	4.81	3.54	5.20	
10.	4.39	3.38	5.01	
11.	4.04	3.23	4.80	
12.	3.76	3.10	4.61	
13.	3.52	2.97	4.42	
14.	3.32	2.86	4.25	
15.	3.14	2.76	4.10	
16.	2.98	2.66	3.97	
17.	2.84	2.57	3.85	
18.	2.72	4.49	3.74	
19.	2.60	2.41	3.63	
20.	2.50	2.33	3.54	
22.	2.31	2.19	3.39	
25.	2.07	2.00	3.18	
30.	1.76	1.73	2.92	
35.	1.56	1.54	2.72	>1.555
40.	1.42	1.41	2.48	>1.135
45.	1.35	1.34	2.44	>1.086
50.	1.30	1.29	2.34	>1.037





TABLE 6. - Continued

m	$\underline{n}_S$	$\underline{n}_R$	$\underline{n}_H$	$\underline{n}_C$
60.	1.23	1.23	2.20	>1.009
70.	1.18	1.17	2.11	>1.003
80.	1.12	1.12	2.04	>1.001
90.	1.09	1.09	1.99	>1.001
100.	1.06	1.06	1.96	>1.000
150.	1.02	1.02	1.87	>1.000
200.	1.01	1.01	1.81	>1.000
300.	1.00	1.00	1.73	>1.000
400.	1.00	1.00	1.64	>1.000
500.	1.00	1.00	1.64	>1.000
1000.	1.00	1.00	1.54	>1.000

### Computer Results for Sulfuric Acid.

The results of the computer program for sulfuric acid are tabulated in Tables 11, 12, and 13, and are illustrated in Figures 5, 6, and 7.

The notation used for the equilibrium "constants" is as follows:

$$K_1 = P C_{\text{HSO}_4^-} / C_{\text{H}_2\text{SO}_4} a_{\text{H}_2\text{O}}^{\underline{n}} \quad (44)$$

$$K_2 = P C_{\text{SO}_4^{2-}} / C_{\text{HSO}_4^-} a_{\text{H}_2\text{O}}^{\underline{n}} \quad (45)$$

$$K_{10} = C_{\text{H}_5\text{SO}_5} / C_{\text{H}_2\text{SO}_4} C_{\text{H}_3\text{O}} \quad (46)$$

$$K_{1n} = C_{\text{H}} (\text{H}_2\text{O})_n C_{\text{HSO}_4^-} / C_{\text{H}_2\text{SO}_4} a_{\text{H}_2\text{O}}^{\underline{n}} \quad (47)$$

$$K_{2n} = C_{\text{H}} (\text{H}_2\text{O})_n C_{\text{SO}_4^{2-}} / C_{\text{HSO}_4^-} a_{\text{H}_2\text{O}}^{\underline{n}} \quad (48)$$

where P is the total concentration of the proton hydrate species,  $\underline{n}$  is the average hydration number of the proton as obtained from Figure 3, n is the integral number of water molecules involved in the particular hydrate under consideration, and the C's are the concentrations of the subscripted



Figure 3. Plot of the average hydration number of the proton,  $\bar{n}$ , vs. concentration of sulfuric acid, predicted by the total water in the system, by Raoult's law and by the idealized  $h_0$  equation, as compared to the computed results.



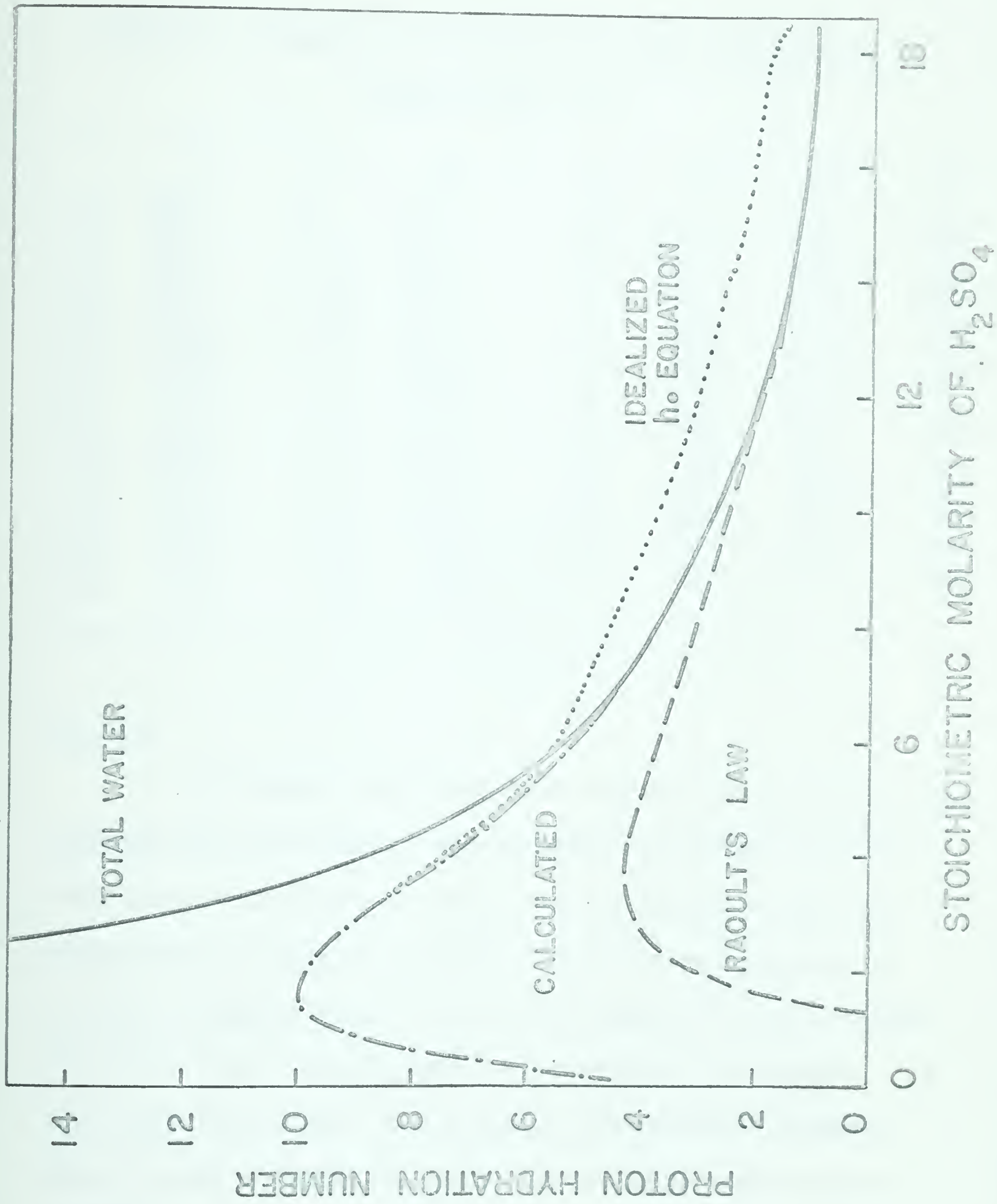






TABLE 7. AVERAGE HYDRATION NUMBER OF THE PROTON  
PERCHLORIC ACID

m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$	m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$
0.1	555.	-27.	36.0	4.0	13.9	6.28	8.05
0.2	278.	-13.	27.1	4.5	12.3	6.19	7.67
0.3	185.	-6.8	24.1	5.	11.1	6.07	7.36
0.4	139.	-4.0	25.3	6.	9.25	5.78	6.68
0.5	111.	-1.8	24.5	7.	7.93	5.48	6.17
0.6	92.5	0.1	22.7	8.	6.94	5.17	5.74
0.7	79.3	0.7	20.6	9.	6.17	4.89	5.49
0.8	70.7	1.2	18.7	10.	5.60	4.61	5.22
0.9	61.7	2.4	17.2	11.	5.05	4.36	4.90
1.0	55.5	3.2	16.1	12.	4.63	4.12	4.61
1.5	37.0	5.8	12.4	13.	4.27	3.90	4.31
2.0	27.8	5.8	10.7	14.	3.96	3.69	4.10
2.5	22.2	6.44	9.54	15.	3.70	3.49	3.88
3.0	18.4	6.36	9.00	16.	3.47	3.32	3.66
3.5	15.9	6.43	8.44				

species.

In the tables, the variation in acceptable values permitted by this method is given; the diagrams show smoothed curves drawn through the lines corresponding to these values. Thus the two entries under each concentration in Tables 11, 12 and 13 correspond to the minimum and maximum acceptable values. The bracketed values at 9, 10, 12, 13 and 14 m sulfuric acid in Tables 11 and 12 were obtained by relaxing the restrictions on the relative concentrations and equilibrium constants. Thus, the only restriction was that all concentrations must be zero or positive.



Figure 4. Plot of the predicted values of the average hydration number of the proton,  $\bar{n}$ , as a function of the concentration of perchloric acid.



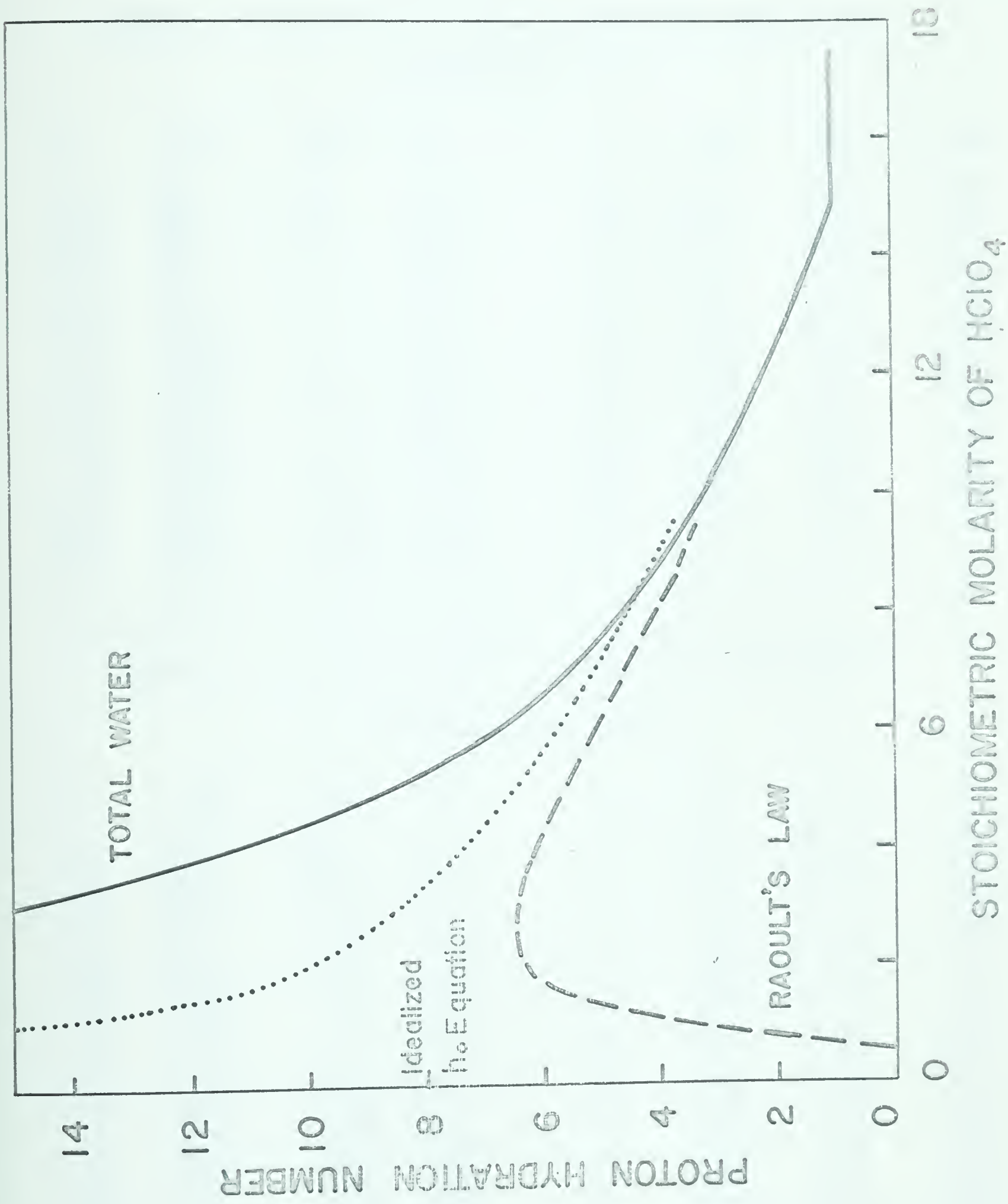






TABLE 8. AVERAGE HYDRATION NUMBER OF THE PROTON

## HYDROBROMIC ACID

m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$	m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$
0.1	555.	-62.	3.6	3.5	15.9	6.78	7.43
0.2	278.	-23.	8.6	4.0	13.9	6.65	7.07
0.3	185.	-13.	9.5	4.5	12.3	6.49	6.76
0.4	139.	-4.	10.5	5.0	11.1	6.32	6.51
0.5	111.	-1.	11.9	6.0	9.25	5.99	5.99
0.6	92.5	2.	11.1	7.0	7.93	5.64	5.56
0.7	79.3	4.	11.0	8.0	6.95	5.29	5.20
0.8	70.7	4.2	11.0	9.0	6.24	5.01	4.91
0.9	61.7	4.9	10.8	10.0	5.68	4.76	4.67
1.0	55.5	5.2	11.0	11.	5.21	4.50	4.51
1.5	37.0	6.1	9.85	12.	4.82	4.27	4.36
2.0	27.8	6.78	9.11	13.	4.48	4.05	4.22
2.5	22.2	6.94	8.37	14.	4.18	3.85	4.10
3.0	18.4	6.88	7.84				

TABLE 9. AVERAGE HYDRATION NUMBER OF THE PROTON

## HYDROCHLORIC ACID

m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$	m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$
0.1	555.	-29.	6.3	4.5	13.2	6.18	7.32
0.2	278.	-14.	8.0	5.	11.9	6.08	7.07
0.3	185.	-6.6	10.0	6.	10.1	5.86	6.55
0.4	139.	-4.2	10.1	7.	8.79	5.61	6.20
0.5	111.	-1.8	11.2	8.	7.81	5.37	5.90
0.6	92.8	0.0	11.9	9.	7.05	5.15	5.54
0.7	79.6	1.3	12.1	10.	6.43	4.92	5.31
0.8	69.7	2.1	11.7	11.	5.93	4.71	5.04
0.9	61.9	2.8	11.5	12.	5.51	4.51	4.87
1.0	55.8	3.34	11.3	13.	5.16	4.34	4.70
1.5	37.5	5.22	10.6	14.	4.85	4.18	4.57
2.0	28.4	6.50	9.52	15.	4.59	4.04	4.39
2.5	22.9	6.12	8.86	16.	4.35	3.89	4.30
3.0	19.2	6.26	8.30	17.	4.15	3.76	4.20
3.5	16.6	6.28	7.90	18.	3.97	3.64	4.11
4.0	14.7	6.26	7.62				



TABLE 10. AVERAGE HYDRATION NUMBER OF THE PROTON

## NITRIC ACID

m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$	m	$\bar{n}_S$	$\bar{n}_R$	$\bar{n}_H$
0.1	557.	-30.	45.3	14.	7.33	4.53	5.94
0.2	280.	-18.	42.8	15.	7.23	4.63	5.75
0.3	187.	-11.	32.2	16.	7.06	4.68	5.55
0.4	141.	-6.8	34.1	17.	6.98	4.75	5.39
0.5	113.	-4.5	31.2	18.	6.92	4.83	5.28
0.6	94.6	-2.7	27.3	19.	6.88	4.91	5.14
0.7	81.4	-1.5	24.8	20.	6.87	5.01	5.02
0.8	71.5	-0.5	22.6	22.	6.89	5.21	4.82
0.9	63.8	0.0	20.8	25.	7.06	5.58	4.56
1.0	57.6	1.0	19.1	30.	7.62	6.33	4.27
1.5	39.2	2.8	15.4	35.	8.39	7.22	4.01
2.0	30.0	3.8	13.6	40.	9.04	7.98	3.80
2.5	24.5	4.2	12.3	45.	9.61	8.64	3.60
3.0	20.8	3.83	11.6	50.	10.1	9.20	3.47
3.5	18.2	3.75	11.3	60.	11.3	10.5	3.26
4.0	16.3	3.89	10.8	70.	12.5	11.8	3.10
4.5	14.8	3.74	10.5	80.	14.0	13.3	2.98
5.	13.6	3.94	9.93	90.	15.7	15.0	2.89
6.	11.8	3.94	9.27	100.	16.9	16.3	2.82
7.	10.6	4.09	8.48	150.	24.5	23.9	2.58
8.	9.68	4.16	7.92	200.	31.5	30.9	2.46
9.	9.00	4.22	7.44	300.	47.6	47.1	2.34
10.	8.48	4.31	7.08	400.	58.3	57.6	2.25
11.	8.08	4.38	6.68	500.	59.8	58.9	2.18
12.	7.77	4.42	6.41	1000.	61.7	60.9	1.99
13.	7.53	4.46	6.18				



TABLE 11.

## SUMMARY OF MOLAR CONCENTRATIONS OF PROTON HYDRATE SPECIES

m	$\text{H}_3\text{O}^+$	$\text{H}_5\text{O}_2^+$	$\text{H}_7\text{O}_3^+$	$\text{H}_9\text{O}_4^+$	$\text{H}_{11}\text{O}_5^+$	$\text{H}_{13}\text{O}_6^+$	$\text{H}_{15}\text{O}_7^+$	$\text{H}_{17}\text{O}_8^+$	$\text{H}_{19}\text{O}_9^+$	$\text{H}_{21}\text{O}_{10}^+$
0.1		0.000 0.006	0.006 0.021	0.040 0.055	0.067 0.071					
0.2			0.000 0.012	0.012 0.047	0.081 0.116	0.120 0.132				
0.3			0.000 0.002	0.002 0.009	0.034 0.040	0.338 0.340				
0.4				0.000 0.016	0.016 0.066	0.168 0.217	0.258 0.275			
0.5				0.000 0.001	0.001 0.003	0.010 0.012	0.618 0.618			
0.6					0.000 0.016	0.016 0.062	0.228 0.274	0.448 0.464		
0.7						0.000 0.008	0.250 0.273	0.290 0.312	0.304 0.312	
0.8						0.000 0.020	0.020 0.079	0.310 0.368	0.584 0.604	
0.9						0.000 0.004	0.004 0.017	0.069 0.081	1.025 1.029	
1.0							0.000 0.068	0.068 0.270	0.401 0.600	0.507 0.573
1.5							0.000 0.005	0.005 0.020	0.054 0.069	1.743 1.747
2.0							0.000 0.024	0.024 0.094	0.137 0.204	2.204 2.226
2.5							0.000 0.002	0.002 0.009	1.256 1.262	1.739 1.741
3.0							0.000 0.243	0.243 0.935	0.956 1.612	1.488 1.694





TABLE II. - Continued

m	$H_3O^+$	$H_5O_2^+$	$H_7O_3^+$	$H_9O_4^+$	$H_{11}O_5^+$	$H_{13}O_6^+$	$H_{15}O_7^+$	$H_{17}O_8^+$	$H_{19}O_9^+$	$H_{21}O_{10}^+$
3.5						0.000 0.043	0.043 0.166	0.640 0.754	3.240 3.276	
4.0						0.000 0.004	0.926 0.939	2.043 2.054	1.603 1.606	
4.5					0.000 0.143	0.143 0.534	0.546 0.901	3.875 3.981		
5.0					0.000 0.240	0.665 1.315	2.131 2.709	1.906 2.075		
6.0				0.000 0.229	0.229 0.832	2.682 3.198	2.690 2.834			
7.0				0.000 0.042	3.605 3.711	2.145 2.232	1.228 1.251			
8.0			1.107 1.138	1.140 2.360	1.219 3.140	1.510 1.601	0.770 0.792			
9.0			(1.6) (2.9)	(0.1) (5.8)	(0.1) (2.4)	(0.1) (3.4)	(0.5) (0.9)			
10.0			(3.1) (4.3)	(0.1) (3.0)	(0.0) (2.2)	(2.2) (2.7)				
11.0		0.818 1.306	1.306 2.433	2.436 3.227	3.467 3.619					
12.0			(5.5) (6.8)	(0.1) (2.9)	(0.1) (2.0)	(0.9) (1.2)				
13.0		(3.6) (4.6)	(0.1) (8.0)	(0.1) (2.2)	(0.1) (4.1)	(0.1) (0.8)				
14.0		(3.0) (5.0)	(0.0) (9.1)	(0.0) (2.8)	(0.0) (2.9)	(0.4) (0.5)				
15.0		4.266 4.573	2.184 2.852	1.770 2.183	1.718 1.770					
16.0		4.232 5.110	2.356 4.240	1.220 2.355	1.091 1.220					



TABLE 11. - Continued

m	$H_3O^+$	$H_5O_2^+$	$H_7O_3^+$	$H_9O_4^+$	$H_{11}O_5^+$	$H_{13}O_6^+$	$H_{15}O_7^+$	$H_{17}O_8^+$	$H_{19}O_9^+$	$H_{21}O_{10}^+$
17.		4.611 5.803	2.326 4.846	0.841 2.324	0.691 0.840					
18.		5.185 6.537	2.202 5.050	0.558 2.201	0.413 0.558					
19.		5.976 7.296	2.007 4.770	0.441 2.005	0.230 0.352					
20.		6.925 8.109	1.778 4.240	0.336 1.708	0.135 0.229					
22.	2.500 3.618	3.261 9.691	1.314 3.260	0.170 2.010	0.060 0.104					
25.	1.668 4.380	3.732 9.259	0.812 3.730	0.709 0.812						
30.	3.753 6.681	3.220 9.133	0.178 3.220	0.122 0.178						
35.	6.196 7.924	3.802 7.275	0.076 1.839	0.019 0.037						
40.	7.981 8.381	4.812 5.614	0.029 0.433	0.002 0.004						
45.	8.730 8.968	4.008 4.485	0.018 0.257	0.001 0.001						
50.	8.973 9.072	3.525 3.723	0.008 0.108	0.000 <sub>2</sub> 0.000 <sub>3</sub>						
60.	8.858 8.904	2.632 2.724	0.004 0.050	0.000 <sub>02</sub> 0.000 <sub>05</sub>						
70.	8.770 8.776	1.869 1.879	0.001 0.006	0.000 <sub>002</sub> 0.000 <sub>007</sub>						
80.	8.639 8.641	1.244 1.248	0.000 <sub>4</sub> 0.002							
90.	8.359 8.359	0.812 0.813	0.000 <sub>2</sub> 0.001							









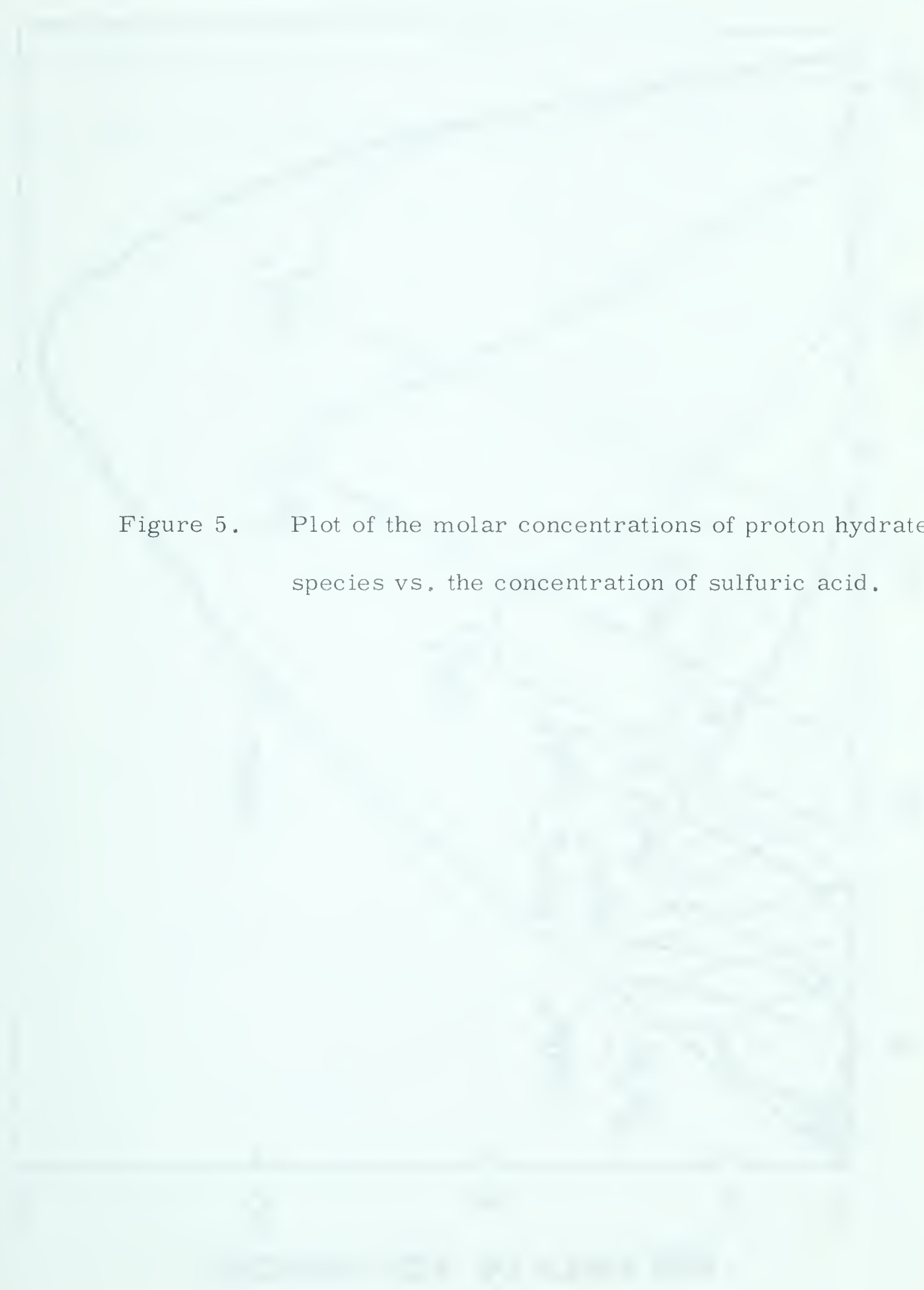


Figure 5. Plot of the molar concentrations of proton hydrate species vs. the concentration of sulfuric acid.



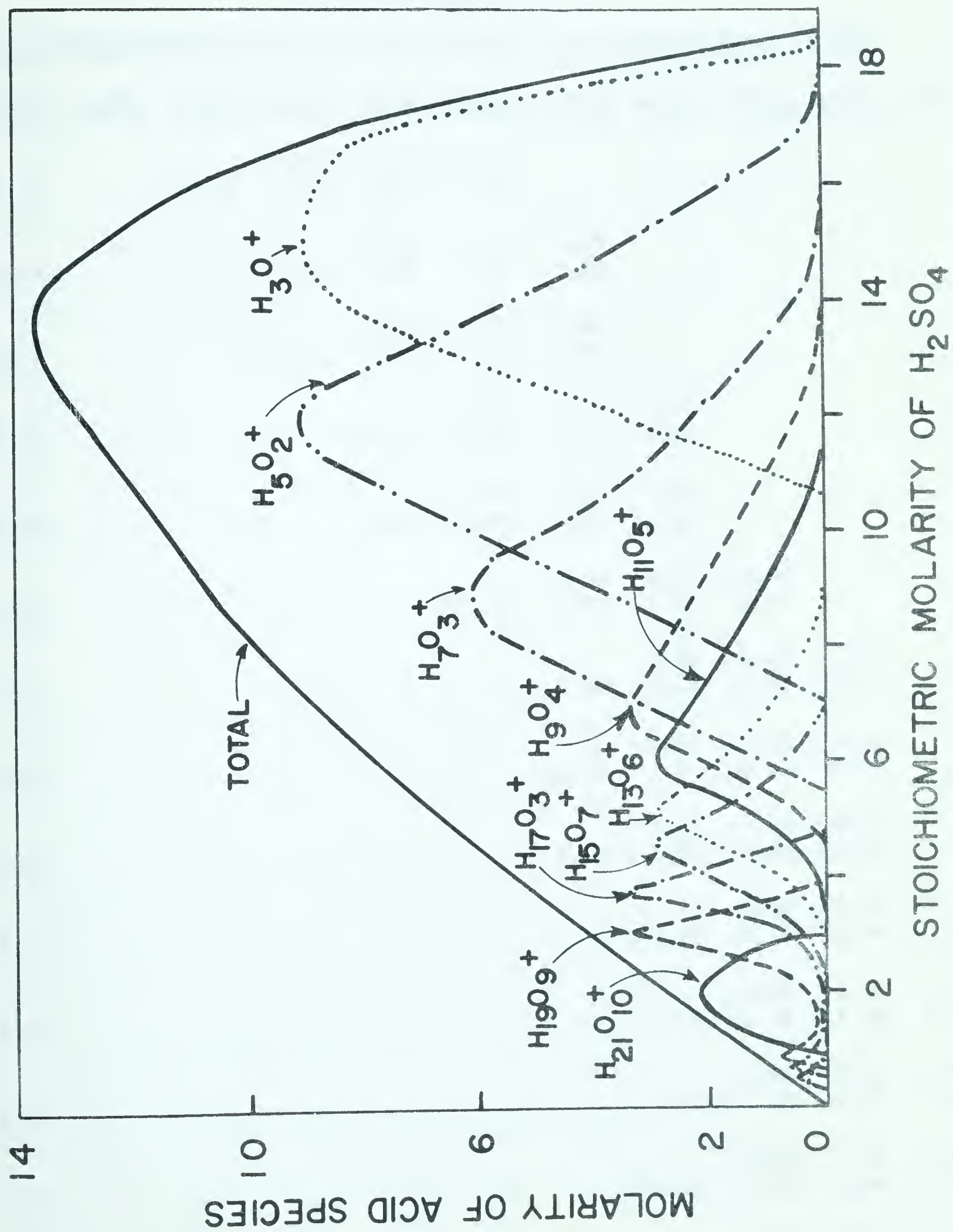




TABLE 12.

SUMMARY OF CONSTANTS FOR EQUILIBRIA INVOLVING  $\text{HSO}_4^-$  --  $\text{SO}_4^{=}$ 

m	$\log K_2$	$\log K_{21}$	$\log K_{22}$	$\log K_{23}$	$\log K_{24}$	$\log K_{25}$	$\log K_{26}$	$\log K_{27}$	$\log K_{28}$	$\log K_{29}$	$\log K_{30}$
0.1				-2.51	-1.69	-1.46					
	-1.17		<-2.54	-1.96	-1.55	-1.44					
0.2					-2.25	-1.41	-1.24				
	-0.91		<-2.26	-1.66	-1.26	-1.20					
0.3					-2.98	-1.83	-0.82				
	-0.77		<-3.01	-2.40	-1.75	-0.82					
0.4						-2.13	-1.12	-0.92			
	-0.63				<-2.14	-1.53	-1.00	-0.90			
0.5						-3.48	-2.35	-0.54			
	-0.53				<-3.50	-2.90	-2.26	-0.54			
0.6							-2.14	-0.96	-0.66		
	-0.44					<-2.15	-1.54	-0.88	-0.36		
0.7								-0.92	-0.84	-0.81	
	-0.36						<-2.43	-0.88	-0.81	-0.80	
0.8								-2.01	-0.80	-0.51	
	-0.29						<-2.02	-1.41	-0.73	-0.50	
0.9								-2.66	-1.44	-0.25	
	-0.21						<-2.67	-2.06	-1.36	-0.24	
1.0									-1.40	-0.61	-0.50
	-0.12							<-1.42	-0.80	-0.44	-0.44
1.5									-2.45	-1.40	0.13
	0.15							<-2.48	-1.86	-1.29	0.14
2.0									-1.59	-0.79	0.45
	0.49							<-1.63	-1.00	-0.62	0.46
2.5									-2.50	0.30	0.49
	0.71							<-2.55	-1.91	0.30	0.49
3.0									-0.30	0.36	0.62
	0.95							<-0.37	0.28	0.59	0.68



TABLE 12. - Continued

m	logK <sub>2</sub>	logK <sub>21</sub>	logK <sub>22</sub>	logK <sub>23</sub>	logK <sub>24</sub>	logK <sub>25</sub>	logK <sub>26</sub>	logK <sub>27</sub>	logK <sub>28</sub>	logK <sub>29</sub>	logK <sub>30</sub>
3.5	1.12							-1.00	0.25	1.05	
							<-1.09	-0.42	0.32	1.05	
4.0	1.30							0.48	0.93	0.93	
							<-1.95	0.48	0.93	0.93	
4.5	1.46						-0.30	0.41	1.39		
						<-0.43	0.27	0.62	1.40		
5.0	1.60						0.51	1.17	1.27		
						<-0.08	0.80	1.27	1.31		
6.0	1.86					0.15	1.42	1.62			
					<-0.06	0.70	1.49	1.64			
7.0	2.08					1.62	1.66	1.67			
					<-0.57	1.63	1.67	1.68			
8.0	2.26			0.75	1.08	1.43	1.84	1.87			
				0.76	1.40	1.84	2.29	1.88			
9.0	2.42			(1.07)	(0.32)	(0.40)	(0.88)	(2.10)			
				(1.33)	(2.02)	(2.02)	(2.55)	(2.35)			
10.0	2.54			(1.53)	(0.37)	(0.64)	(2.71)				
				(1.68)	(1.97)	(2.27)	(2.79)				
11.0	2.66		0.61	1.32	2.10	2.76					
			0.82	1.59	2.22	2.78					
12.0	2.75			(2.12)	(0.82)	(1.27)	(3.04)				
				(2.20)	(2.41)	(2.81)	(3.18)				
13.0	2.84		(1.46)	(0.60)	(0.97)	(1.66)	(3.19)				
			(1.56)	(2.44)	(2.52)	(3.43)	(3.34)				
14.0	2.91		(1.48)	(0.37)	(1.01)	(1.81)	(3.40)				
			(1.70)	(2.66)	(2.86)	(3.57)	(3.51)				
15.0	2.97		1.73	2.21	2.88	3.64					
			1.76	2.32	2.98	3.65					
16.0	3.02		1.82	2.40	2.95	3.74					
			1.90	2.66	3.24	3.78					





TABLE 12. - Continued

m	logK <sub>2</sub>	logK <sub>21</sub>	logK <sub>22</sub>	logK <sub>23</sub>	logK <sub>24</sub>	logK <sub>25</sub>	logK <sub>26</sub>	logK <sub>27</sub>	logK <sub>28</sub>	logK <sub>29</sub>	logK <sub>30</sub>
17.			1.96	2.56	3.02	3.84					
	3.07		2.05	2.88	3.46	3.92					
18.			2.10	2.70	3.07	3.90					
	3.11		2.20	3.06	3.66	4.04					
19.			2.26	2.82	3.20	3.95					
	3.15		2.35	3.20	3.86	4.14					
20.			2.42	2.93	3.31	4.01					
	3.17		2.49	3.30	4.01	4.24					
22.		0.94	2.28	3.12	3.46	4.23					
	3.21	1.10	2.75	3.51	4.53	4.48					
25.		0.86	2.63	3.38	4.74						
	3.24	1.28	3.02	4.05	4.80						
30.		1.37	3.02	3.47	5.02						
	3.21	1.62	3.47	4.73	5.18						
35.		1.69	3.46	3.75	5.13						
	3.13	1.80	3.74	5.13	5.42						
40.		1.96	4.04	4.11	5.29						
	3.15	1.98	4.10	5.28	5.57						
45.		1.97	4.09	4.23	5.38						
	3.00	1.98	4.13	5.37	5.66						
50.		1.94	4.18	4.22	5.32						
	2.87	1.94	4.21	5.32	5.60						
60.		1.77	4.22	4.26	5.13						
	2.57	1.77	4.24	5.13	5.39						
70.		1.45	4.01	4.03	4.80						
	2.10	1.45	4.02	4.78	5.05						



Figure 6. Plot of the logarithm of the equilibrium constants for  $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-}$  equilibria vs. the concentration of sulfuric acid. Notation as described in the text.



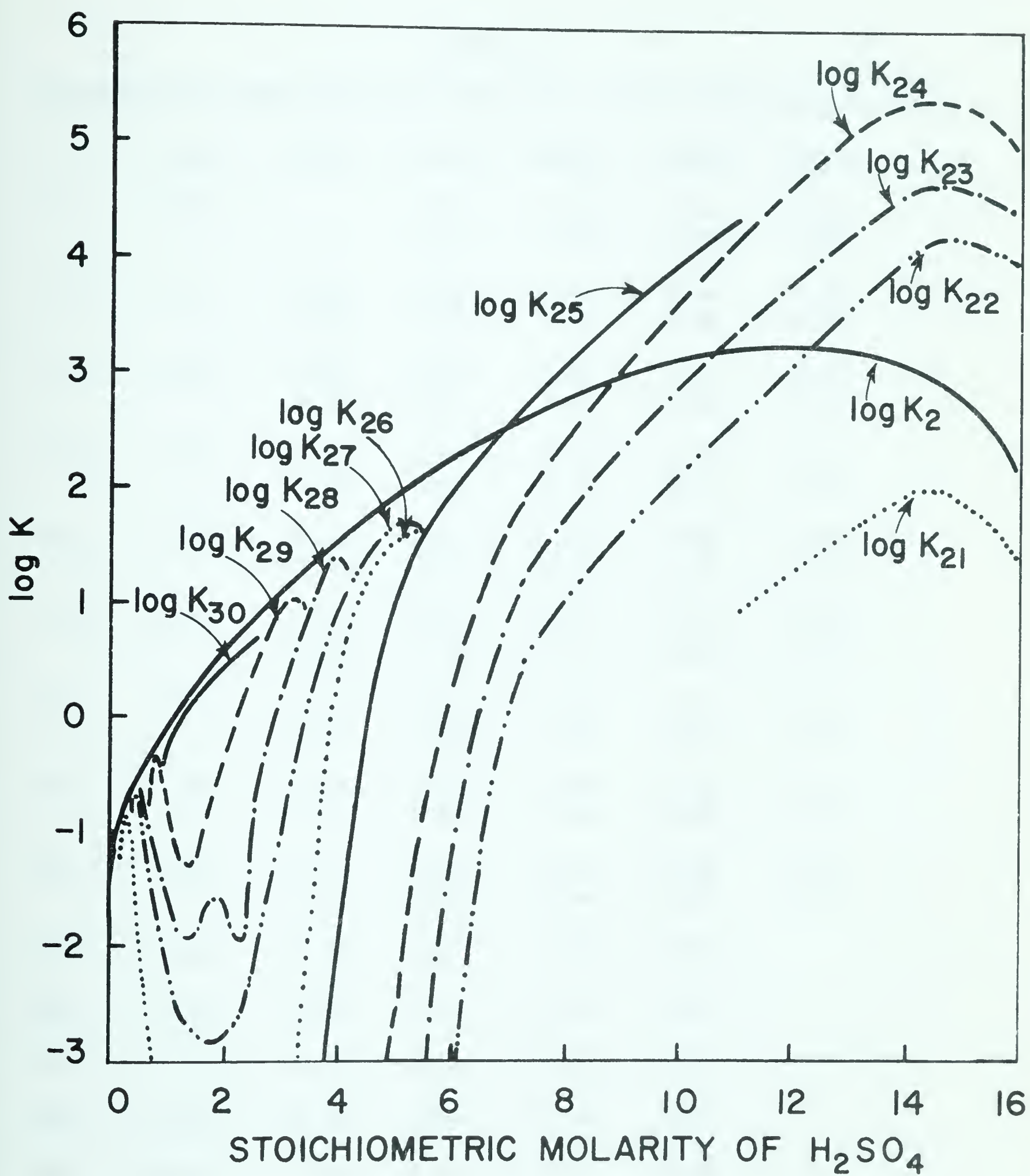






TABLE 13.

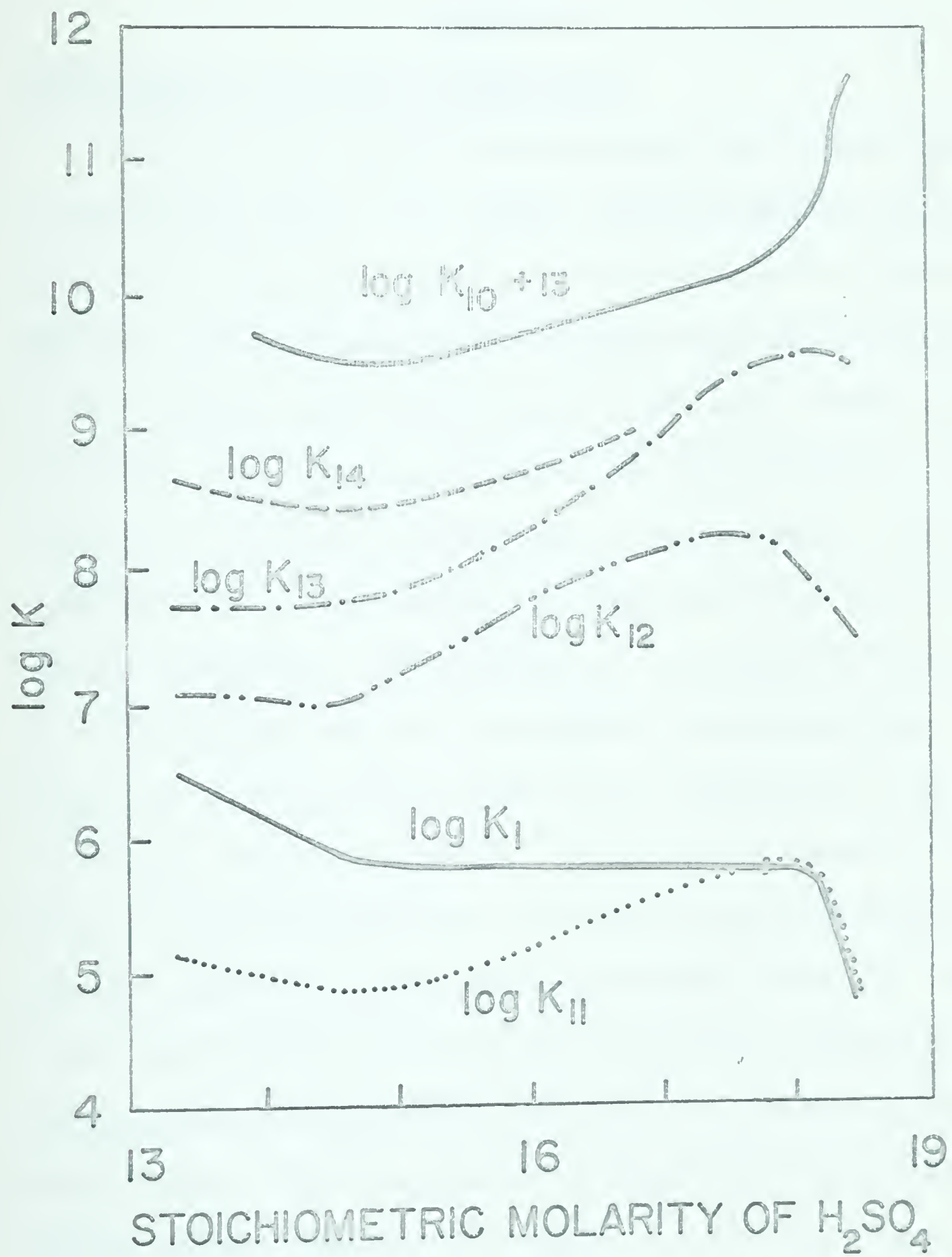
SUMMARY OF CONSTANTS FOR EQUILIBRIA INVOLVING  $\text{H}_2\text{SO}_4$  --  $\text{HSO}_4^-$ 

m	$\log K_1$	$\log K_{10}$	$\log K_{11}$	$\log K_{12}$	$\log K_{13}$	$\log K_{14}$
35.	6.47	-	5.03	6.80	7.08	8.46
		-	5.13	7.08	8.46	8.75
40.	6.19	-3.31	5.00	7.07	7.14	8.32
		-3.28	5.02	7.14	8.32	8.60
45.	5.89	-3.47	4.87	7.03	7.12	8.26
		-3.49	4.88	7.07	8.26	8.54
50.	5.82	-3.51	4.89	7.14	7.17	8.27
		-3.50	4.89	7.16	8.27	8.56
60.	5.80	-3.43	5.00	7.45	7.46	8.35
		-3.42	5.00	7.46	8.35	8.63
70.	5.80	-3.29	5.15	7.71	7.73	8.49
		-3.29	5.15	7.71	8.48	8.75
80.	5.78	-3.21	5.29	7.89	8.02	8.61
		-3.21	5.29	7.89	8.59	8.84
90.	5.76	-3.15	5.40	7.99	8.25	8.71
		-3.15	5.40	7.99	8.65	8.90
100.	5.74	-3.10	5.48	8.04	8.30	8.78
		-3.10	5.48	8.04	8.78	9.00
150.	5.75	-2.90	5.67	8.14	9.35	
200.	5.79	-2.75	5.75	8.14	9.47	
300.	5.79	-2.52	5.78	7.99	9.55	
400.	5.65	-2.22	5.65	7.88	9.56	
500.	5.13	-1.58	5.13	7.49	9.55	
1000.	4.78	-1.37	4.78	7.74	9.48	



Figure 7. Plot of the logarithm of the equilibrium constants for  $\text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^-$  equilibria as a function of sulfuric acid concentration. Notation as described in the text.







## DISCUSSION

Criticism of the Bascombe and Bell Model

There are a number of dubious assumptions involved in the Bascombe and Bell model.<sup>11</sup> For example, the stoichiometric acid concentration was used throughout as the total concentration of the proton hydrate species, completely neglecting the secondary dissociation of sulfuric acid and the incomplete dissociation of hydrochloric acid. Further, as the authors point out, hydration of all species other than the proton was neglected, and water in these solutions was assumed to be monomeric. However, undoubtedly the worst assumptions are those which were made regarding activity coefficients, in particular the use of the Setschenov equation for  $f_B$ . The Setschenov equation is an empirical relationship which is often found to be valid up to about 1 M electrolyte concentration,<sup>12</sup> but its "derivation" contains assumptions<sup>12</sup> which cannot be expected to be valid in more concentrated solutions. Data on the activity coefficients of some Hammett indicators in  $H_2SO_4$  have been published recently,<sup>54</sup> and the results show that the neutral indicators are salted-in rather than salted-out at acid concentrations greater than about 2 to 3 M; that  $f_B$  varies appreciably from indicator to indicator although their structures are quite similar; and that in general the Setschenov equation is not a good approximation to the behavior of  $f_B$  over any very wide concentration range. For simpler aromatic molecules, salting-in at higher acid concentrations does not always occur,<sup>55</sup> but the Setschenov equation is not valid over a wide electrolyte concentration range in this case either.





These observations mean that the Bascombe and Bell model is only as good as their second approach, which relies on the assumptions that  $f_{H^+(H_2O)_n} = f_{BH^+}$  and that  $f_B = f_{H_2O}^n$ . It is unlikely that either of these assumptions would be valid. In the first, the charge effect would be expected to cancel, but  $f_{H^+(H_2O)}$  refers to a species which is present in relatively large amounts, particularly at high acid concentrations, whereas  $BH^+$  is present in trace quantities. Thus interactions between  $BH^+$  ions should be negligibly small, but interactions between hydrated protons are very likely important. Further, the comparison is between a hydrated species,  $H^+(H_2O)_n$ , and an unhydrated species,  $BH^+$ . This implies that hydration of  $BH^+$  has no effect on  $f_{BH^+}$ , which is very unlikely. The second assumption can be assessed for  $H_2SO_4$  by the use of Boyd's data,<sup>54</sup> which shows that for mono-nitroanilines such as are used in dilute and moderately concentrated acid,  $f_B$  increases up to about 3 M  $H_2SO_4$ , and then decreases. It is difficult to predict accurately the behavior of  $f_{H_2O}$ , but if it is kept in mind that anion hydration and water structure are neglected, and that  $f_{H_2O}$  refers to the stoichiometric water in the solution less the water of proton hydration, it is obvious that  $f_{H_2O}$  must decrease with increasing acid concentration, at least initially. The difference in behavior of  $f_B$  and  $f_{H_2O}$  would be amplified by raising  $f_{H_2O}$  to a positive power. Thus, the second assumption cannot be valid in sulfuric acid, although it may be better in perchloric and hydrochloric acids where less extensive data suggests that the indicators may be salted-in at very low acid concentrations.<sup>64, 65</sup>



In summary , it appears that the Bascombe and Bell model gives sufficiently good agreement with the experimental data to suggest that the basic idea, the inclusion of a factor involving the activity of the water, is sound, but a closer look at some of the assumptions involved suggests that the model is capable of refinement.

#### Wyatt's Model and the Acidity Function as a Function of the Activity of Water.

The present results for concentrated sulfuric acid do not differ qualitatively from Wyatt's.<sup>13</sup> He explained the high acidity by a contribution from  $\text{H}_5\text{O}_2^+$ , whereas in the present work, both  $\text{H}_5\text{O}_2^+$  and  $\text{H}_7\text{O}_3^+$  were considered in very concentrated sulfuric acid. The difference shows clearly that neither is a unique solution, and that it is not possible to tell which is correct, if either is, without recourse to some additional information.

Wyatt also noticed that " . . . the acidity function of solutions of all completely ionized acids should be a common function of the water activity only." <sup>13</sup> If there is no error in the acidity function data quoted in Tables 1 to 5, this statement is not quite true. A more accurate statement would be, "Plots of the Hammett acidity function vs. the activity of water for sulfuric, hydrochloric, hydrobromic and perchloric acids over the range for which data is available, and nitric acid from 0 to 8 M, can be represented within  $\pm 0.15$  logarithmic units by a single curve." In 8 M nitric acid,  $\Delta = 0.6$  which would cause the deviation from the curve for the other acids. Also, both the  $\text{H}_\text{O}^{52}$  and  $\text{a}_{\text{H}_2\text{O}}^{21, 50}$  data are less reliable for nitric acid than for the other acids. The





corresponding plots of the  $H_R$  data for sulfuric<sup>66</sup>, perchloric<sup>67</sup> and nitric<sup>67</sup> acids do not show the same general behavior, as was first pointed out by Hogfeldt.<sup>60</sup> The curves for  $H_R$  in sulfuric and in nitric acids can be represented by one line  $\pm 0.25$  logarithmic units when plotted against  $a_{H_2O}$ , but the behavior of perchloric acid is entirely different. These facts suggest that the most important factor in determining the  $H_O$  acidity function is the activity of water, and that the rather subtle changes in environment which may be caused by changing the anion causes either minor changes in  $f_B$  and  $f_{BH^+}$ , or at least changes which tend to cancel out, while with the  $H_R$  function, the anion causes either far larger changes in  $f_{ROH}$  and  $f_{R^+}$ , the activity coefficients of the  $H_R$  indicator and the carbonium ion derived from it, or quite different changes in the two activity coefficients. The changes in activity coefficients of the Hammett indicators will be discussed more fully later.

#### Comparison of Hogfeldt's Model with the Present Work.

The most obvious failing of the model proposed by Bascombe and Bell<sup>11</sup> is that since a fixed hydration number was used, the model is not applicable at high acid concentrations where there is not sufficient water in the solution to form a species as highly hydrated as that assumed in moderately concentrated acid. Both Hogfeldt's<sup>19-22</sup> and the present model attempt to overcome this difficulty by the use of a variable hydration number. The two models are quite dissimilar in formalized approach, but since both attempt to do the same thing, the basic problems are much





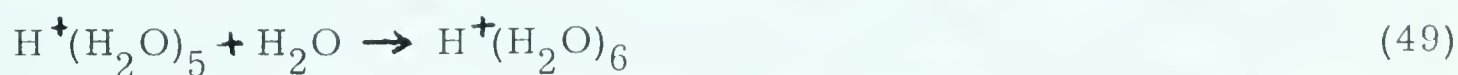
same. The most critical step is the evaluation of an average proton hydration number, or alternatively the evaluation of the total amount of water of proton hydration. In order to do this, it is necessary to make an assumption about the activity coefficients of the proton, the Hammett indicator B and its conjugate acid  $\text{BH}^+$  -- or at least about the ratio  $f_{\text{H}^+} f_{\text{B}} / f_{\text{BH}^+}$ . The same kind of data -- acidity function, activity of water and dissociation data -- were used in both models, in many cases from the same sources, so the two models would be expected to give the same results. This seems to be approximately true as far as the average hydration numbers are concerned. The present model does have the advantage that while Hogfeldt expects his average hydration numbers to be less accurate in dilute solution,<sup>19</sup> in our own work the use of an essentially empirical quantity for the total water of proton hydration means that the results for sulfuric acid should be about as reliable in dilute solution as they are in concentrated acid. In fact, the assumption that the activity coefficient ratio is unity is better in dilute solution. This advantage is to a large extent cancelled out by uncertainties in the experimental data which will be described later.

A comparison of Hogfeldt's most recent paper<sup>22</sup> and the computer results for sulfuric acid shows the most striking differences between the two models. Hogfeldt has assumed that the best result is that involving the least number of proton hydrate species, and mainly for reasons of symmetry he has selected the species  $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$ ,  $\text{H}_9\text{O}_4^+$



and, presumably as a best fit of the remainder,  $\text{H}_{23}\text{O}_{11}^+$ . From symmetry considerations,  $\text{H}_{21}\text{O}_{10}^+$  would have been more logical. In the present work, it was assumed that the best result was that requiring the least hydrated species and no species was disallowed. The best model probably lies somewhere between these two extremes -- it seems reasonable that  $\text{H}_9\text{O}_4^+$ , for instance, would be favored because of its high degree of symmetry, but on the other hand, it is highly unlikely that  $\text{H}_{23}\text{O}_{11}^+$  would be the next stable hydrate species above  $\text{H}_9\text{O}_4^+$ , and that  $\text{H}_7\text{O}_3^+$  would not exist at all.

The most recent mass spectrometric evidence<sup>54</sup> indicates that the heats of hydration of proton hydrate species decrease in a regular fashion, with no special preference being shown for  $\text{H}_9\text{O}_4^+$ . Hydrates up to  $\text{H}_{15}\text{O}_7^+$  were detected, but the absence of higher hydrates was apparently a matter of instrumental sensitivity rather than proof of non-existence of higher hydrates. The enthalpies of hydration were considerably larger than would be expected from the work of Wicke, Eigen and Ackermann<sup>4</sup> -- for instance,



had an enthalpy of -24.4 kcal. / mole, as opposed to the value of -4.9 predicted from the temperature dependence of the partial molar volume and partial molar heat capacity. However, to quote the authors of the mass spectral results, "We cannot discuss these results further since they (the values of the enthalpy of hydration) are highly tentative and equilibrium conditions may not be present."<sup>54</sup>



Hogfeldt also required that the equilibrium constants be true constants,<sup>22</sup> whereas in this work the equilibrium "constants" were permitted to drift on the implicit assumption that at least part of the drift was caused by the neglect of the activity coefficients of the proton hydrate, acid and anion.

### Criticism of the Present Model.

It was assumed in the present work that  $h_0$  is the simple sum of contributions from the various proton hydrate species present. There are two questionable assumptions in this statement. First, it was assumed that all of the proton hydrate species have the same acid strength, which is probably not true. However, it is difficult to assign relative values. For instance,  $H_9O_4^+$  has six equivalent protons which are not involved in hydrogen bonding and thus are available to a proton acceptor as compared to three in  $H_3O^+$  and hence on a statistical basis would be expected to be twice as strong an acid, but its "conjugate base",  $(H_2O)_4$ , has four acceptor sites available, three of which are involved in hydrogen bonding as well as covalent bonds, as opposed to one site in  $H_2O$ . It would also be expected that the larger aggregate would be resonance stabilized. Considering these three factors, it is difficult to decide the order of the acidity of the proton hydrate species, let alone the relative values.

The second assumption involved in the use of a simple sum to represent  $h_0$  is that acids other than the hydrated proton need not be considered. For instance,  $HSO_4^-$  and / or  $H_2SO_4$  are present at all of the acid concentrations considered. The contribution to the acidity of an acid HA





would be of the form

$$\gamma_{\text{HA}} h_o = K_{\text{HA}} m_{\text{HA}} f_{\text{HA}} f_{\text{B}} / K_{\text{H}^+(\text{H}_2\text{O})_n} m_{\text{A}^-} f_{\text{A}^-} f_{\text{BH}^+} \quad (50)$$

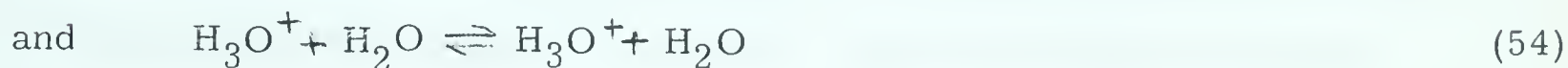
corresponding to the equilibrium



where the  $m$ 's are molal concentrations and the  $f$ 's are activity coefficients of the subscripted species, and the ratio  $K_{\text{HA}} / K_{\text{H}^+(\text{H}_2\text{O})_n}$  gives the acid strength of HA relative to the hydrated proton, defined by equations such as



$$K_{\text{HA}} = a_{\text{H}_3\text{O}^+} a_{\text{A}^-} / a_{\text{HA}} a_{\text{H}_2\text{O}} \quad (53)$$



$$K_{\text{H}^+(\text{H}_2\text{O})} = a_{\text{H}_3\text{O}^+} a_{\text{H}_2\text{O}} / a_{\text{H}_3\text{O}^+} a_{\text{H}_2\text{O}} = 1 \quad (55)$$

The significant quantity is  $\gamma_{\text{HA}} h_o / h_o$ . By ignoring all of the activity coefficients,  $\gamma_{\text{HSO}_4^-} h_o / h_o$  and  $\gamma_{\text{H}_2\text{SO}_4} h_o / h_o$  can be calculated from the data in Table 1, using Wyatt's value of 2550 for  $K_{\text{H}_2\text{SO}_4}^{15}$  and the thermodynamic value of  $K_{\text{HSO}_4^-} = 0.0120$ .<sup>55</sup> For  $\text{HSO}_4^-$ , it was found that  $\gamma_{\text{HSO}_4^-} h_o / h_o$  decreases from about 0.02 in 1 M acid to  $3 \times 10^{-7}$  in 11 M, while  $\gamma_{\text{H}_2\text{SO}_4} h_o / h_o$  varies from  $6 \times 10^{-6}$  in 15 M acid to  $8 \times 10^{-7}$  in 18.5 M. The numerical values are subject to considerable error arising from relatively small errors in the concentrations of the acid and its conjugate base, but it seems certain that the contributions to the acidity of acids other than the hydrated proton are negligible.





As can be seen from the values of the average hydration number of the proton given in Table 6, there is a marked difference between the values of  $\bar{n}_H$  and  $\bar{n}_C$ . These are both average hydration numbers derived from idealized  $h_o$  equations, equations (31) and (33). The difference arises because of the different way in which the average is defined. In equation (31), the contribution of each species is calculated, and then these contributions are summed to give the acidity. The average hydration number  $\bar{n}_C$ , is then obtained by dividing the total concentration of water of proton hydration by the total concentration of hydrated proton. On the other hand, equation (33) gives  $\bar{n}_H$ , the number of water molecules which must be associated with each proton in order to give the observed acidity -- i.e. it assumes that there is only one proton hydrate species present. The former is the more reasonable model, since in general the single species model will involve a non-integral hydration number. Further, as can be seen in Table 6,  $\bar{n}_H$  has values in moderately concentrated solution which are larger than the composition of the solution permits, while  $\bar{n}_C$  approaches a reasonable limit. The reason for this difference is that as the activity of water decreases more highly hydrated species contribute proportionably more to the acidity. As a very simple example, consider a solution containing only 1 m  $H_3O^+$  and 1 m  $H_5O_2^+$ , and where  $a_{H_2O} = 0.1$ . Hence,  $P = 2$  m,  $Q = 3$  m, and  $\bar{n}_C = 1.5$ . Using equation (31) with  $h_o = 110$ ,  $\bar{n}_H = 1.7$ . As the activity of water approaches unity, the difference between the two methods disappears.



The importance of the number of species considered can also be seen by a comparison of Table 6 to Tables 11 and 12. Table 6 shows that the three species model fails over the range 9 to 30 m. The four species model is not entirely satisfactory in the region from 9 to 14 m as shown in Tables 11 and 12, but does give solutions. The model could undoubtedly be improved further by considering even more proton hydrate species.

The most unsatisfactory aspect of the hydration approach to the problem of the behavior of strong acids is the necessity of an assumption regarding activity coefficients. This is equally true of the Bascombe and Bell model,<sup>11</sup> Hogfeldt's model<sup>19-22</sup> and the present model. In both of the latter two, it was assumed that the logarithm of the activity coefficient ratio  $f_B f_{H^+(H_2O)_n} / f_{BH^+}$  is negligibly small. This is not entirely a matter of choice, since it is suggested mainly by the fact that attempts to correct for it seem to apply a correction in the wrong direction.<sup>11, 56</sup>

In the case of sulfuric acid, Boyd's data give some information about two of the three factors involved.<sup>56</sup> The interpretation of the experimental results for the uncharged indicator is straightforward, and although the measurements are not extensive enough to apply an exact correction over the entire range, it is at least possible to estimate the size of the effect. Using  $h_o$  values which have been corrected for the activity coefficient of the basic indicator in the idealized  $h_o$  equation (33) gives values of  $\underline{n}_H$  which are lower than those in Table 6, at least for





moderate concentrations. A maximum is still present near 1.5 m, but the highest value is about 8 instead of the value of 10 found previously. The two calculations give the same value at infinite dilution and at between 4 and 4.5 m, and at higher acid concentrations the correction for  $f_B$  increases the average hydration number.

The interpretation of the experimental data for the salts of the indicators must involve an additional assumption.<sup>68</sup> Hence, Boyd's values for  $f_{BH^+}$  are relative to the activity coefficient of the tetraethyl ammonium ion,  $TEA^+$ . The assumption is that  $f_{TEA^+} = 1$  over the entire acid concentration range studied, since there are no groups present which can interact specifically with the solvent. It is possible to make some other assumption which would lead to different values of the activity coefficients. The following is no more than speculation, but provides a plausible basis for an entirely different assumption.

As will be discussed in more detail later, the present results suggest that water clusters cease to be important at acid concentrations greater than about 2 to 3 M. Assuming for the moment that this is the case, the behavior of the activity coefficients of neutral molecules can perhaps be explained on the basis of clathrate type cages similar to those which have been proposed for the structure of pure water.<sup>57</sup> With simple aromatic molecules such as benzene,<sup>58</sup> the activity coefficient increases linearly with sulfuric acid concentration up to about 2 to 3 M sulfuric acid, and then seems to remain constant. If these molecules exist in solution within some sort of a clathrate cage,<sup>59</sup> the ability of water to form such cages should be closely





related to its ability to form clusters. As the acid concentration increases the cage and cluster forming ability of the water must decrease, at least eventually, if for no other reason than the decreasing volume concentration of water. Hence the experimental data suggests that benzene's solubility in pure water is due to the formation of clathrate cages and that as acid is added, these cages are destroyed, decreasing the solubility. Thus the solubility reaches a minimum value with the complete destruction of cages and then remains constant with increasing acid concentration. The Hammett indicators differ from benzene in that they contain one or more groups which interact specifically with the acid.<sup>56</sup> This tends to salt-in the indicator, i.e. increase its solubility or decrease its activity coefficient. In the case of the mono-nitro indicators, both effects are present, leading to a maximum in the plot of activity coefficient vs. acid concentration -- the molecule is salted-out by the destruction of cages and salted-in by a specific interaction with the acid. The former effect is more important in dilute acid and the latter in more concentrated solutions. This type of behavior, although not as marked, is also observed with anisole.<sup>58</sup> When more than one nitro-group is present, the salting-in effect is larger and leads to a net salting-in even at very low acid concentrations.<sup>56</sup>

If this is the reason for the observed behavior of the activity coefficients of uncharged hydrocarbons in aqueous acid, what would one predict to be the behavior of a charged hydrocarbon? The purpose of using a large ion such as  $\text{TEA}^+$  as a reference is to prevent the possibility of close approach of a water molecule to the atom bearing the charge.



The fact that specific hydration is impossible does not rule out the possibility of hydration by a clathrate cage, in which case the activity coefficient of an ion such as  $\text{TEA}^+$  would be expected to behave in a fashion quite similar to an uncharged molecule -- i.e. increase moderately up to an acid concentration of a few molar, and then presumably remain at least approximately constant at higher acid concentrations. It is not possible to predict how large this effect would be, but qualitatively the effect would be to increase the values of  $f_{\text{BH}^+}$  as given by Boyd.<sup>56</sup> This would lead to an approximate cancellation of  $f_{\text{B}}$  and  $f_{\text{BH}^+}$  in the region below about 2 to 3 M acid, and a net increase in the average proton hydration number over the entire acid concentration range.

Unfortunately, although it is possible to apply a reasonably accurate correction for  $f_{\text{B}}$  over a fairly wide range and to at least see the qualitative effect of changes in  $f_{\text{BH}^+}$ , the third factor in the activity coefficient ratio,  $f_{\text{H}^+(\text{H}_2\text{O})_n}$ , remains completely unknown. The evaluation of this factor from the existing activity coefficient data for strong acids would have to take into consideration such effects as incomplete dissociation, the difference between the true single ion activity coefficient and the mean ionic activity coefficient, and hydration. Such a calculation is too arbitrary at present to be of much practical value, and in any case is really just an alternative approach to the same problem as discussed in the present work.

Since it is not possible to correct exactly for the factor  $f_{\text{H}^+(\text{H}_2\text{O})_n} f_{\text{B}} / f_{\text{BH}^+}$ , the simplest assumption possible has been made, i.e. that the factor is unity over the entire range. This is very unlikely





to be true, but is probably as close to the truth as any other assumption which could be made at the present time, and it has the virtue of being the easiest assumption to apply. The same problem is encountered in dealing with the equilibrium "constants" given in Tables 12 and 13, and was dealt with in the same way, by making the assumption that the ratio of the activity coefficients is unity. Molal concentrations were used throughout the calculations; this is an arbitrary decision based on the observation that slightly lower values of the average proton hydration number  $\bar{n}_H$  resulted. The curves of the average hydration number vs. the concentration of acid were very little different in either shape or position when molar units were used for the total proton concentration. Hence the choice of concentration units does not seem to be critical.

#### Reliability of the Calculations .

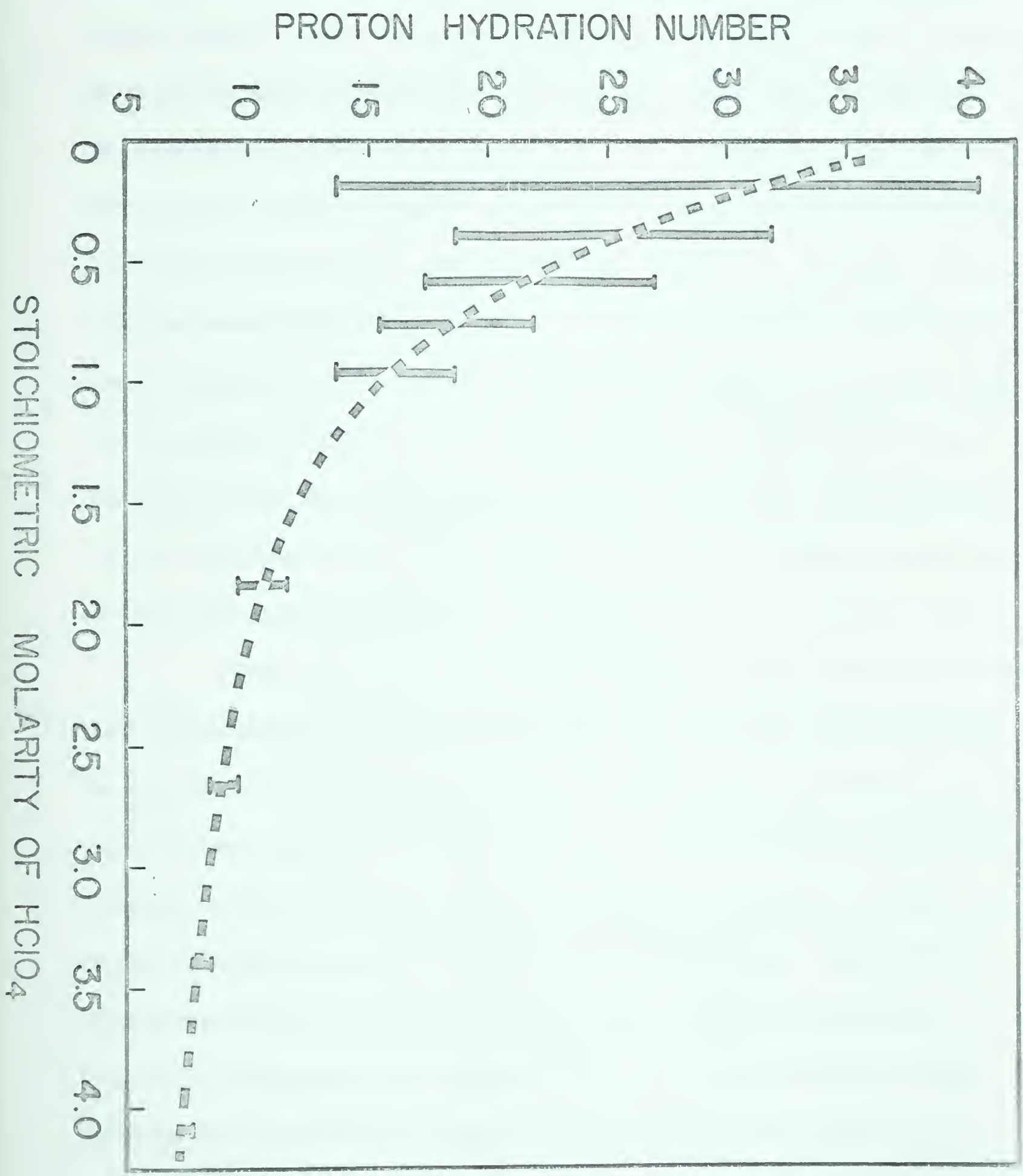
As pointed out in the previous section, the model is not entirely satisfactory from the point of view of the assumptions necessary, but it is not possible to estimate how reliable these assumptions are. Error can also arise from the experimental data, but in general it is possible to predict its magnitude and effect. The only important experimental sources of error are the  $h_o$  and dissociation data. Figure 8 shows the results on  $\bar{n}$  of a small error in  $H_o$ . This is the most important source of error in dilute solution. The vertical lines show the range of values of  $\bar{n}_H$  obtained when  $H_o$  for  $HClO_4$  is based on a  $pK_A$  of  $0.99 \pm 0.04$  for p-nitroaniline. The higher values correspond to the lower values of  $pK_A$ . Thus, the high values of the proton hydration numbers in dilute solution are quite



Figure 8. The variation in  $\underline{n}_H$  for perchloric acid caused by an error of  $\pm 0.04$  logarithmic units in  $H_O$ .









possibly caused by the use of a  $pK_A$  which is a few hundredths of a logarithmic unit too small. It should be noted that although this type of error makes it virtually impossible to draw any meaningful conclusions about the average hydration number below about 1 M, it does not have any serious effect on the results at higher acid concentrations. The error in the graphical interpolation of  $H_O$  is also appreciable in the 0 to 1 M region, leading to an increased probable error in  $H_O$ . The value of  $\underline{n} = 4$  at infinite dilution of  $H_2SO_4$  was not obtained directly from the data, but assumed, and the  $H_O$  values "corrected" to give a smooth curve. This involved an adjustment of less than 0.02 logarithmic units in any case. The estimated error in the data is about  $\pm 0.02$ ,<sup>14</sup> and allowance must also be made for error in the dissociation data.<sup>7, 16</sup>

The only other important experimental source of error is in the total concentration of the proton hydrate species,  $P$ . As is the case for  $h_O$ , this is most important in dilute acid and least important in more concentrated solutions. However, the value of  $P$  must approach the stoichiometric molarity of acid in dilute solution, i.e. as  $\alpha \rightarrow 1$ , so there is a smaller probable error in  $P$  at low acid concentrations. The vertical lines drawn in along the curve of  $\alpha$  vs. acid concentration for HCl, Figure 2, correspond to an error of  $\pm 50\%$  in the concentration of undissociated acid. This error leads to an error of less than  $\pm 2\%$  in  $\underline{n}_H$ .

Of the three methods used to determine  $P$  or  $\alpha$  for the various acids, the Raman spectral procedure<sup>7, 16</sup> is certainly the best. It would of course be desirable to have more significant figures in the results,



but there is no serious doubt as to the validity of the method. The same cannot be said of the NMR method.<sup>17, 18, 41</sup> The problems presented by the method have been thoroughly reviewed.<sup>60</sup> In the present study, the NMR results for nitric acid have been accepted since they are in agreement with the Raman results,<sup>7</sup> and are in fact dependent on the Raman work for the evaluation of one of the two constants involved.<sup>18</sup> The NMR results for perchloric acid have been rejected for the reasons given in the Calculations section. The interpretation of the NMR data is based on the assumption that the chemical shift is determined by three species only -- solvent water, whose shift is assumed to remain constant at all acid concentrations; the oxonium ion,  $\text{H}_3\text{O}^+$ , neglecting any further water of hydration; and undissociated acid. In the case of perchloric acid, the chemical shift of the undissociated acid was obtained from measurements on the pure anhydrous acid,<sup>17, 18</sup> and it has since been suggested that anhydrous perchloric acid is a mixture of  $\text{HClO}_4$ ,  $\text{Cl}_2\text{O}_7$ ,  $\text{H}_3\text{O}^+$  and  $\text{ClO}_4^-$ .<sup>35</sup> Hence, there are several possible causes for the unreasonably low values found for  $\alpha$ : a large shift on the breakdown of water structure, neglect of water of hydration of the oxonium ion and / or the anion, or error in the shift of the undissociated acid. Probably all of these factors are important to some extent. The fact that the change of chemical shift with concentration does not give the same value for all acids on extrapolation to infinite dilution<sup>17, 18, 41, 61</sup> suggests that perhaps some effect of the anion is the most important factor.<sup>60</sup>





The third method which has been used to determine the extent of dissociation, the Hogfeldt plot,<sup>46</sup> is open to question. It is based on the assumption that the behavior of the activity coefficient ratio  $f_{H^+} f_B / f_{BH^+}$  is the same for all of the strong acids. This could only be justified by experimental data. As seen in Figure 1, the present data does not entirely support the conclusion, but with the exception of nitric acid, the plots are very similar. It is difficult to tell at present whether or not the difference between the three curves for perchloric acid, sulfuric acid, and hydrochloric / hydrobromic acids is real. The last two acids lie in a common curve very nearly exactly midway between those for perchloric and sulfuric acids. Error in  $H_0$  has virtually no effect on these curves, since it is involved on both axes. It might be sufficient to show a common curve for all of the acids in dilute solution. Hogfeldt has shown that the values of  $\alpha$  for hydrochloric acid are consistent with the existing NMR data,<sup>17</sup> but in view of the discussion above this is of doubtful importance.

It should be pointed out that these plots are not sensitive functions of the proton concentration, and conversely are not capable of giving accurate values of  $P$ . Thus the error of  $\pm 50\%$  in the concentration of undissociated hydrochloric acid, shown in Figure 2, is not unreasonably large. However, the values obtained by the Hogfeldt method do seem to be reasonable, and since no other method is at present available for hydrobromic and hydrochloric acids, the results have been tentatively accepted.



### The Change in the Structure of the Solvent with Increasing Acid Concentration.

As can be seen from an inspection of the results for the average hydration numbers of the proton, something is definitely not right in dilute solution. We believe that one of the main problems is the fact that the structure of the solvent has been neglected. The importance of water structure was first suggested by the maximum in  $\bar{n}_H$  in sulfuric acid, which will be discussed in the next section. This section deals with some of the evidence suggesting that water structure ceases to be important at about 2 to 4 m acid.

The behavior of  $\bar{n}_R$ , the average hydration number of the proton calculated from Raoult's law using equation (32), is consistent with the disappearance of water clusters at a moderate concentration of acid. With all of the acids considered here, the hydration number is large and negative in dilute solution, increases rapidly with increasing acid concentration, and takes on reasonable values and behavior at between 2.0 and 4.5 m acid. The simplest way to explain this behavior is to assume that Raoult's law is at least approximately valid over the entire range of acid concentrations, and that the apparent failure in dilute solution is caused by the use of an expression which does not consider the effect of water structure. In order to apply a correction for water structure, it would be necessary to know, or rather at the present time to assume, values for the fraction of the total water involved in the solvent polymer and the size of the polymeric unit in pure water. In addition, it would be necessary to make some assumption about the rate of change of both of these quantities as a function of acid





concentration. In view of the uncertainty in the first two quantities,<sup>27, 28</sup> and the complete lack of knowledge of the effect of increasing acid concentration, the calculation does not at present appear worthwhile.

In the case of the monobasic acids, the values given as  $\underline{n}_R$  can be better considered to be the total hydration numbers of the electrolyte. The results then suggest that the hydration numbers of the anions fall approximately in the order  $\text{Cl}^- \simeq \text{Br}^- > \text{ClO}_4^- > \text{NO}_3^-$ , which is reasonable. It is not possible to make a direct comparison between sulfuric acid and the monobasic acids in this respect since the secondary dissociation and resulting non-equality of the proton and anion concentration complicates the statement of Raoult's law when both proton and anion hydration are considered.

As can be seen from Table 10, the values of  $\underline{n}_R$  for nitric acid are entirely unreasonable at high acid concentrations. However, if the Raoult's law expression is set up on the assumption that only the undissociated acid is hydrated, values of the hydration number of the undissociated acid are reasonable (less than about 3) at acid concentrations above 15 m. In order to obtain the hydration number of the undissociated acid, it is assumed that the "free" water, i.e. the fraction of the water which gives the observed partial pressure, is equal to the total stoichiometric concentration of water less the concentration of water of hydration of the undissociated acid. The values of  $\underline{n}_R$  obtained from equation (32) assume that the "free" water is the total concentration of water minus the water of hydration of the proton. Thus, hydration of the undissociated acid





is probably the main reason for the unrealistic values of  $\underline{n}_R$  obtained in concentrated nitric acid. Unfortunately, it is not possible to solve Raoult's law expression which allows for hydration of both the proton and the undissociated acid.

In summary, Raoult's law used in a form which considers the species actually present rather than the stoichiometric composition of the system appears to be approximately valid at acid concentrations greater than about 2.0 to 4.5 m, depending on the acid. Since the present use of Raoult's law assumes that the solvent water is monomeric, the validity has been taken as evidence for the disappearance of polymeric water in the region of 2.0 to 4.5 m, and the failure of Raoult's law in dilute solution can be attributed to the presence of water clusters.

Any major changes in the structure of the solvent should also be reflected in the change in the activity of water with acid concentration. Plots of the activity of water,  $a_{H_2O}$ , vs. the concentration of acid are sigmoid shaped. At acid concentrations up to a few molal, the activity of water changes only slightly. The activity then decreases rapidly with increasing acid concentration, and finally approaches zero asymptotically at very high acid concentrations. This behavior can be interpreted as follows. The initial slowly changing portion of the curve corresponds to a region of monomer-cluster equilibrium, in which most of the monomeric water which is removed as water of hydration is replaced by the breakdown of water clusters. The center region reflects the disappearance of monomeric water as water of hydration in a region in which no clusters



are present, and hence there is no source to replenish the supply of monomer. Finally, at high acid concentrations, essentially all of the water is involved in hydration and the observed vapor pressure is regulated by the equilibrium between free water and water of hydration, the hydrate being favored. This interpretation implies that the point at which the clusters disappear can be obtained from the shape of the curve. Specifically, clusters should cease to be important at the concentration at which the second derivative of the activity of water vs. acid concentration curve is a minimum -- i.e. at the point at which the slope is changing most rapidly. Frank<sup>26</sup> points out that cluster formation is a cooperative phenomenon, the formation of one hydrogen bond aiding the formation of the next. Hence, a fairly abrupt transition is to be expected between the regions where clusters are or are not present.

There are two possible ways in which the position of the minimum in the second derivative could be found -- by fitting the data to an algebraic equation and finding the concentration at which  $d^3 a_{H_2O} / d m_{HA}^3 = 0$ , or numerically by taking second differences as a function of acid concentration and reading the point graphically. The former procedure would definitely be preferred if the correct form of the equation were known. Unfortunately, it is not. Attempts were made to fit the data for sulfuric, perchloric and hydrochloric acids to an equation of the form

$$a_{H_2O} = 1 + A m_{HA} + B m_{HA}^2 + C m_{HA}^3 + D m_{HA}^4 \quad (56)$$

This is the simplest power series which has a third derivative involving the acid concentration. A least squares procedure was used which involved





successive corrections to the residuals.<sup>62</sup> The only definite conclusion which can be drawn is that it is not possible to fit the experimental data exactly to this equation. The numerical procedure was then attempted, giving the result shown in Figure 9 for sulfuric acid. Similar plots for perchloric and hydrochloric acids showed too much scatter to permit any definite conclusion to be drawn. The numerical procedure requires exceedingly precise data, and even then yields meaningful results only if a relatively large concentration increment (1 m in Figure 9) is used. Thus, the investigation of the change in the activity of water as a function of acid concentration is consistent with the postulate that water clusters disappear at about 1 to 2 m sulfuric acid. However, the numerical method used is not capable of yielding a more exact number, nor does it give any useful information about the other acids.

A further indication that water structure disappears at a low acid concentration is given by recent measurements of the heat of solution of a number of organic bases in varying concentrations of sulfuric acid.<sup>63</sup> Using a range of strong to very weak bases, it was found that the partial molal enthalpy of solution of the base passes through a minimum at about 25% sulfuric acid (3.5 m). It appears that drastic changes in the structure of the solvent are masking any interaction of the organic base and the acid. Hence it seems certain that whether or not the present interpretation is correct, major changes are occurring in the solutions between 0 and 4 m sulfuric acid.

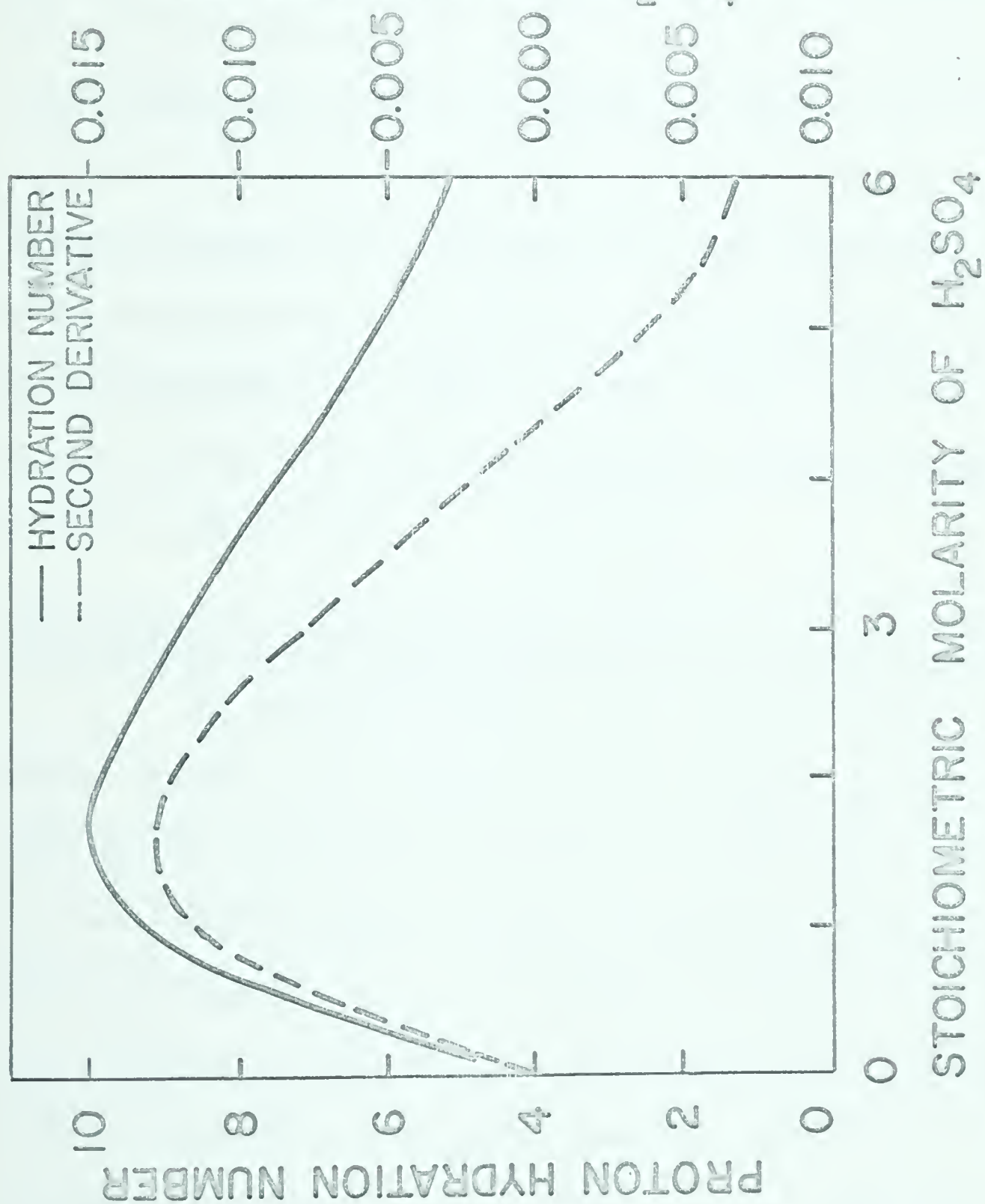




Figure 9. The second derivative of the activity of water in sulfuric acid with respect to the stoichiometric molality of acid, as compared to  $\underline{n}_C$ .



# SECOND DERIVATIVE OF $a_{H_2O}$ VS. MOLARITY OF $H_2SO_4$





Thus, three separate approaches are all consistent with the disappearance from solution of water clusters in moderately concentrated acid. Sulfuric acid is the only acid of the five under consideration for which data, or sufficiently precise data, is available for the use of all three methods. The concentration of sulfuric acid at which clusters are predicted to disappear is different in each case - - 1.5 m from the second derivative of the activity of water, 3.5 m from the heats of solution data, and about 4.5 m from the hydration number of the proton calculated from Raoult's law. It is difficult to know which of these concentrations, if any, is correct, so it is perhaps best at this point to say that water structure is expected to become negligible at  $3 \pm 1.5$  m sulfuric acid.

#### The Maximum in the Proton Hydration Number in Sulfuric Acid.

An unexpected maximum was observed in the proton hydration number obtained from the Hammett acidity function,  $\underline{n}_H$  or  $\underline{n}_C$  (Table 6 and Figure 3). Several different approaches were used in order to test the reality of this maximum, which was observed at a concentration of about 1.5 m sulfuric acid. First, Tables 7 to 10 show that maxima are also obtained in the plots of  $\underline{n}_H$  vs. acid concentration in hydrobromic acid (at 0.5 m) and in hydrochloric acid (at 0.7 m), but do not seem to be present in perchloric or nitric acids. However, these observations must be regarded with suspicion in view of the effect on the hydration number of a small error in the acidity function, which was shown in Figure 8. For instance, if the true values of  $H_0$  correspond to the lower





ends of the vertical lines shown in Figure 1, a maximum is then observed at about 0.5 m perchloric acid. On the other hand, it is possible that the maxima observed in hydrobromic and hydrochloric acids are in fact artifacts resulting from a small error in the acidity function data. It is not likely that the maximum observed in the case of sulfuric acid is a result of experimental error in the acidity function, since the  $H_0$  data has been confirmed by several independent workers. Also, the maximum occurs at a higher acid concentration where the effect on the hydration number of error in  $H_0$  is small. The fact that more reasonable values of  $\bar{n}_H$  are obtained in very dilute solutions of the monobasic acids in which maxima are observed indicates that the results for hydrobromic and hydrochloric acids are more reliable than those for perchloric and nitric acids in the dilute region, and hence suggests that the hydration number also goes through a maximum in the case of the monobasic acids.

The situation that must be explained is that a maximum in the apparent hydration number is observed in sulfuric acid, and if maxima occur in the other acids, they seem to be at a considerably lower acid concentration. The extent of hydration of the proton in relatively dilute acid solutions is the result of a balance of at least two opposing effects -- the breakdown of water structure and the resultant decrease in the dielectric constant of the solution, and the decrease in the concentration of available water. In dilute solution, the amount of monomeric water decreases very slowly, and the decrease in the dielectric constant possibly could give a net increase in the extent of hydration. At higher acid concentrations,



the decrease in the amount of monomeric water is much more rapid and hence becomes the more important factor. The sulfate ion is the only divalent species considered and would be expected to have a greater structure-breaking effect than the monovalent anions. The disappearance of water clusters at a lower concentration of sulfuric acid than of the monobasic acids, coupled with and reflected by the larger decrease in the dielectric constant in sulfuric acid solutions<sup>69</sup> would lead one to expect maxima at higher concentrations of the monobasic acids. However, at higher acid concentrations the decrease in the amount of monomeric water present may be sufficient to completely eliminate the maxima. Unfortunately, the data on the change of dielectric constant with acid concentration is not extensive, and the statement made above about the relative decrease in the dielectric constant of water on the addition of different acids rests on measurements in hydrochloric acid<sup>69</sup> and values for the other acids estimated on the assumption that an additivity law is valid.

Thus, on the basis of the values of the apparent hydration number calculated from the Hammett acidity function, one would expect either no maximum or a maximum in  $\bar{n}$  at a low concentration of monobasic acid, in particular at a concentration of less than 1.5 m. However, consideration of the structure-breaking effect and the decrease in dielectric constant indicates that if a maximum in  $\bar{n}$  exists in the monobasic acids, it should occur at an acid concentration greater than 1.5 m. Neither of these two methods can be considered to be very reliable at the present time. It can be said that there is a subtle balance of forces between effects





favoring hydration and water cluster formation and effects tending to destroy these structures, and it is possible that the balance of forces is considerably different for different strong acids. As yet the experimental data is neither precise enough nor extensive enough to draw any definite conclusions about differences in the behaviour of various strong acids.

A second test of the reality of the maximum in the apparent hydration number involved the calculation of an average apparent hydration number of the proton from other acidity functions. This involved the use of an idealized acidity function equation completely analogous to equation (31). The other functions used were the  $H_R$  function of Deno and co-workers,<sup>66</sup> Arnett and Mach's  $H_O'''$  function,<sup>70</sup> Boyd's  $H_-$  function,<sup>71</sup> and the  $G$  function of Michaelis and Granick.<sup>72</sup> The values of  $\underline{n}$  obtained from these functions are shown in Figure 10, along with the values of  $\underline{n}_H$  from the  $H_O$  equation and the values of the hydration number assuming all of the water in the solution is hydrating the proton--i.e., the ratio of the stoichiometric concentration of water to the concentration of the proton. This is the upper limit of acceptable values of the hydration number.

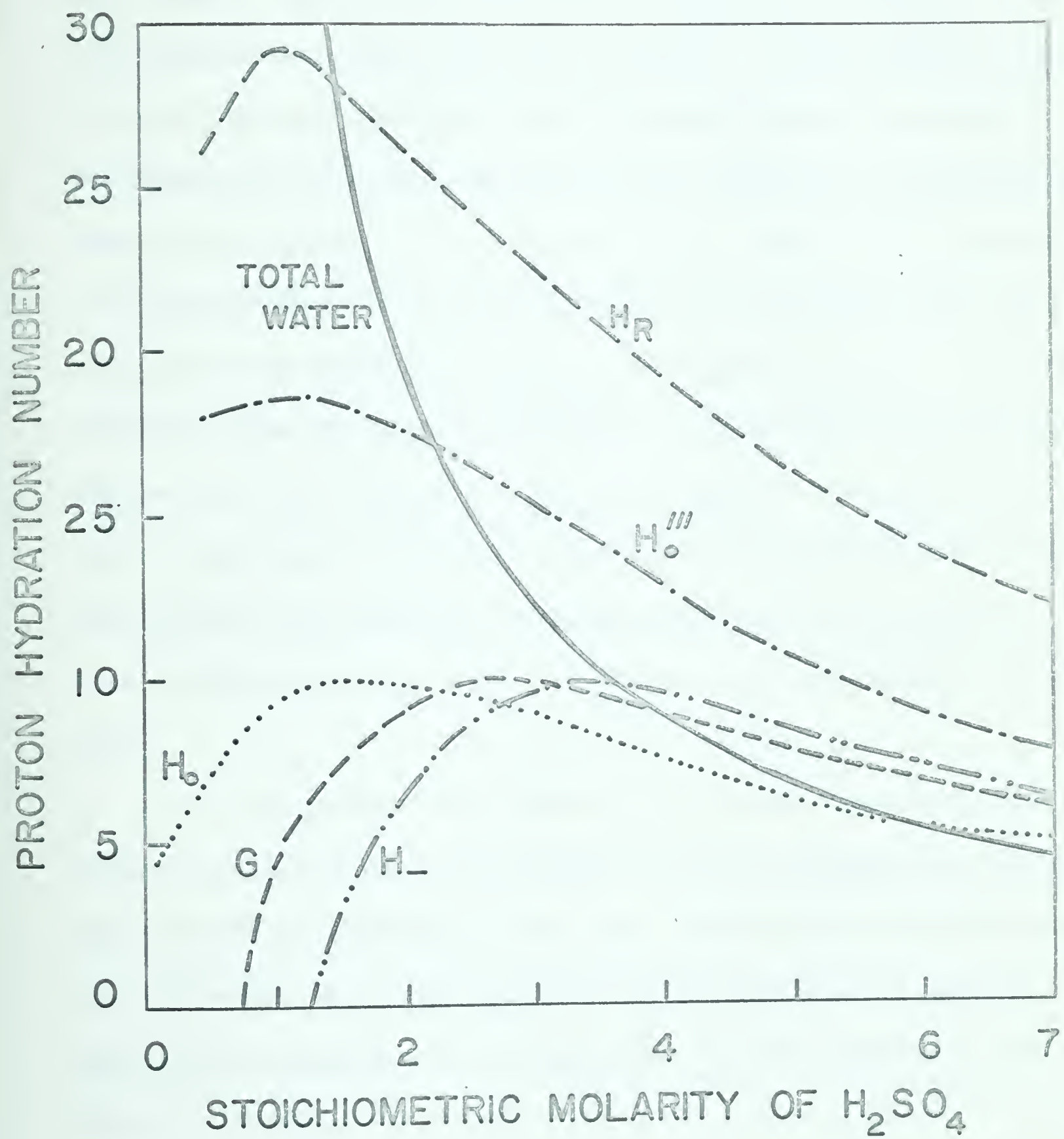
There are several interesting facts shown by Figure 10. First, the apparent hydration number passes through a maximum no matter which acidity function is used, and furthermore the maximum occurs at about  $2 \pm 1$  M  $H_2SO_4$ . Second, three of the five acidity functions-- $H_O$ ,  $H_-$  and  $G$ --predict a maximum value of the apparent hydration number of  $9.91 \pm 0.06$ . Agreement of this order can only be regarded as fortuitous, but the agreement between acidity functions based on indicators as different a primary





Figure 10. The average hydration number of the proton in sulfuric acid as calculated from the  $H_O$ ,  $H_O'''$ ,  $H_R$ ,  $H_-$  and G acidity functions.







nitroanilines, cyanocarbons and thiazines is rather remarkable. From the small amount of data available at present,<sup>56</sup> it seems that the behavior of the activity coefficient of the neutral indicator species is similar for the nitroanilines and cyanocarbons, but quite different for the arylmethanols used to determine  $H_R$ . If the indicator activity coefficient ratio behaves in the same fashion for all of the various types of indicators used, the maximum in the apparent hydration number could be an artifact, but this would be a rather remarkable coincidence. It would seem more reasonable that the maximum, whether it be real or an artifact, is caused by the activity coefficient of the proton, and that the observed variation of size and position of the maximum is caused by differences in the behaviour of the activity coefficients of the various indicators and their conjugate acids.

It is perhaps worth repeating at this point that the use of  $H_O$  values corrected for the activity coefficient of the uncharged base using Boyd's data<sup>56</sup> also predicted a maximum. In this case, the highest value of  $\bar{n}$  was smaller than in the case of the uncorrected  $H_O$  data, but the position was unchanged--i.e. the maximum value of  $\bar{n}$  was found to at about 1.5 m  $H_2SO_4$ .

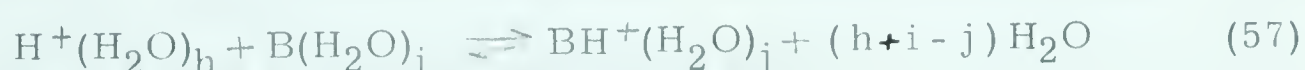
The third point of interest shown by Figure 10 is that all of the acidity functions used predict values of the apparent hydration number in concentrated acid which are larger than permitted by the composition of the solution. At least part of this behavior is caused by the difference between a single species acidity function equation and a multi-species





equation, as was discussed earlier with reference to  $\underline{n}_H$  and  $\underline{n}_C$  from the Hammett acidity function. However, it should be noted the the Hammett acidity function is the best behaved from the point of view of yielding acceptable values of the apparent hydration number, since it predicts physically possible values of  $\underline{n}$  up to the highest acid concentration of any of the acidity functions investigated. The  $H_R$  function is the worst in this respect, but it differs in that the indicator equilibrium does not involve a simple proton transfer like the other indicators undergo, and also that, as first pointed out by Högfeltdt,<sup>73</sup>  $H_R$  is a very different function of the activity of water for several strong acids. It will be interesting to see the results of further studies on strong acids other than sulfuric and to see whether  $H_R$  or  $H_O$  is the special case in plots of this type.

There are two ways in which the indicator could give a maximum in the apparent hydration number of the proton as an artifact. The effect of the experimental activity coefficients has been shown above to reduce but not eliminate the maximum, assuming that Boyd's interpretation of the experimental data for the activity coefficients of the conjugate acids of the indicators is correct<sup>56</sup>. The second effect which must be considered is that of a change in the stoichiometry of the indicator equilibrium caused by differences in the hydration of the indicator and its conjugate acid. A more general form of the indicator equilibrium than was given in the Calculations section would be



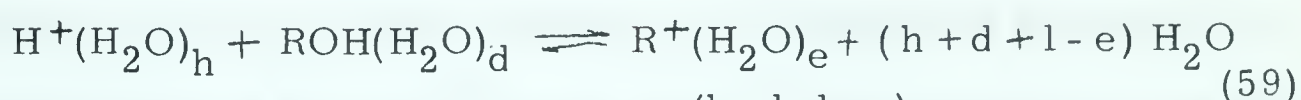
The corresponding definition of  $h_O$  would then be



$$h_o = a_{H^+(H_2O)_h} f_{B(H_2O)_i} / a_{H_2O}^{(h+i-j)} f_{BH^+(H_2O)_j} \quad (58)$$

Equation (58) reduces to the same form as used in the present model if  $i = j$ . The true hydration number of the proton,  $h$ , is used since equation (57) involves only true chemical species while previously it was assumed that  $i = j = 0$ . If the hydration numbers of the indicator and its conjugate acid are equal,  $h = \bar{n}_H$ . Otherwise, the quantity we have called the average apparent hydration number of the proton is actually  $h + i - j$ .

The corresponding equations for the  $H_R$  function are



and 
$$h_R = a_{H^+(H_2O)_h} f_{ROH(H_2O)_d} / a_{H_2O}^{(h+d+1-e)} f_{R^+(H_2O)_e} \quad (60)$$

where ROH is the  $H_R$  indicator and  $R^+$  is the carbonium ion derived from it. Taking logarithms of equations (58) and (60) and subtracting gives

$$\begin{aligned} H_R - H_o = & \log f_{B(H_2O)_i} - \log f_{ROH(H_2O)_d} + \log f_{R^+(H_2O)_e} \\ & - \log f_{BH^+(H_2O)_j} + (j + d + 1 - i - e) \log a_{H_2O} \end{aligned} \quad (61)$$

Taft<sup>74</sup> assumed that the sum of the first four terms of equation (61) was zero, i.e. that the activity coefficients cancel. He also assumed that  $k = d = i = 0$ , or that  $BH^+$  is the only one of the four indicator species appearing in this scheme to be hydrated. These two assumptions reduce equation (61) to

$$H_R - H_o = (j - 1) \log a_{H_2O} \quad (62)$$

and hence  $j$ , the hydration number of  $BH^+$ , can be obtained from the slope of a plot of  $H_R - H_o$  against the logarithm of the activity of water. Taft found a value of  $j = 4$  in 52 to 62 % sulfuric acid.





If  $i \approx 0$  and  $j \approx 4$  as suggested by Taft, the activity of water is raised to a very small positive, zero or even negative power in equation (58), which reduces or eliminates the most obvious contribution to the high acidity of acid solutions. The assumption that ROH is unhydrated is suspect;<sup>75</sup> if ROH is hydrated the observed slope from a plot of  $H_R - H_O$  vs.  $\log a_{H_2O}$  would be  $j + d + 1$ , and hence  $j$  would be less than 4 in this concentration range.

Arnett and Mach<sup>70</sup> have applied Taft's treatment over the range 0 to 70% sulfuric acid, and have modified and extended the treatment to include comparisons of  $H_R$  to  $H_O'''$  and  $H_O$  to  $H_O'''$ . They found that the values obtained for  $j$  or the corresponding hydration numbers from the other two comparisons vary greatly with the acid concentration. Hence, the integral value of  $j \approx 4$  is probably a coincidence arising from the particular rather narrow concentration range used by Taft.

Arnett and Mach point out that for Taft's treatment to be valid, the sum of the logarithms of the activity coefficients in equation (61) need only be constant over a limited range.<sup>70</sup> If for the moment it is assumed that only  $BH^+$  is hydrated, equation (62) can be written in the more general form

$$H_R - H_O = F(C_{H_2SO_4}) + (j + 1) \log a_{H_2O} \quad (63)$$

when  $F(C_{H_2SO_4})$  represents the variation in the sum of the logarithm of the activity coefficients as a function of the acid concentration. The slope of a plot of  $H_R - H_O$  vs.  $\log a_{H_2O}$  is  $d F(C_{H_2SO_4}) / d \log a_{H_2O} + (j + 1)$ .

Hence, it should be possible to estimate  $F(C_{H_2SO_4})$  from the existing data<sup>56</sup>,





but in view of the experimental uncertainties, it is doubtful that the accuracy of the method would be much improved. However, the method will be more reliable at higher acid concentrations where the logarithm of the activity of water is changing more rapidly. In dilute acid solutions, the method fails in much the same way as does the calculation of  $\bar{n}_H$  in the present model -- the difference between  $H_R$  and  $H_O$  becomes small and hence relatively small errors in the experimental data can cause large errors in the hydration number.

It seems likely that the assumption that the activity coefficients remain constant will not cause any appreciable error in the value of the hydration number in the region where the acid concentration is high enough that the error in the experimental data is small. The assumption that the  $H_O$  indicator base and both forms of the  $H_R$  indicator are unhydrated is a more serious source of error. Equation (61), neglecting the activity coefficient terms but allowing for hydration of all of the indicator forms, becomes

$$H_R - H_O = [(j - 1) + (d - c) + 1] \log a_{H_2O} \quad (64)$$

It is necessary to decide on a definition of hydration at this point -- does it include only water specifically bound to some particular site, as is implicitly understood for water of hydration of the proton, or does it include water in a cage structure such as was discussed in connection with the activity coefficients of the Hammett indicators? Both possibilities will be considered in the following discussion. If cage hydration does occur, it is probably only important in the range from 0 to 3 or 4 m



sulfuric acid. The more important influences on the formation of cages probably include the size and geometry of the species within the cage. Although it is difficult to predict any specific hydration number, these influences would give a minimum difference between the hydration of the Hammett indicator and its conjugate base, since the addition of a proton to a relatively large aromatic molecule will have virtually no effect on either the size or geometry. On the other hand, the removal of  $\text{OH}^-$  from the  $\text{H}_\text{R}$  indicator will result in a major change in the geometry of the molecule, which could result in entirely different types of hydration cages, or in cage hydration of one of  $\text{ROH}$  or  $\text{R}^+$ , and hydration of specific sites in the other. Thus the properties of both the  $\text{H}_\text{O}$  and the  $\text{H}_\text{R}$  indicators are more consistent with the slope of the  $\text{H}_\text{R} - \text{H}_\text{O}$  vs.  $\log a_{\text{H}_2\text{O}}$  plot being identified with changes in the hydration of the  $\text{H}_\text{R}$  indicator forms.

In more concentrated acid solutions, any hydration must involve the interaction of water with specific acceptor sites in the indicators. The most important sites in the nitroanilines are the protons on the amine nitrogen. There are two of them in the indicator base, and three in the conjugate acid. The positive charge in the acid form also favors higher hydration of  $\text{BH}^+$ , but resonance in B will tend to minimize the charge effect. Neglecting any secondary hydration, it might be expected that  $j - i = 1$  if there were sufficient water available to saturate all of the potential hydration sites. As the water activity is reduced, the charge effect would be expected to increase the difference between  $j$  and  $i$ . In the case of the  $\text{H}_\text{R}$  indicators, the best hydration site is the alcoholic





proton in ROH. There is no corresponding site in  $R^+$ . Hence, neither form would be expected to be highly hydrated, but if any hydration occurs, it should occur in ROH rather than in  $R^+$ . The fact that the slopes of plots of the differences in acidity functions vs. the activity of water approach unity at high acid concentrations<sup>70</sup> may be at least partly caused by the cancelation of the quantities  $j - i$  and  $d - e$ .

In summary, it is possible that in dilute acid most of the rather large value of the slope of plots of  $H_R - H_O$  vs.  $\log a_{H_2O}$  may be caused by changes of hydration of the  $H_R$  indicator forms. In more concentrated acid, the difference between the hydration numbers of  $BH^+$  and B may be larger than indicated by the plots. However, as long as the manner of hydration of B and  $BH^+$  is the same, the acid form will be at least as highly hydrated as the basic form, and any error introduced into the present work by the neglect of indicator hydration will lead to low values of the proton hydration number. Thus the maximum in the apparent proton hydration number is probably not caused by the neglect of hydration of the indicators.

### Summary.

It is possible to account for all of the acidity of moderately concentrated strong acids on the basis of hydration of the proton. In the case of sulfuric acid, the same model can be used from 0.1 to 1000 m, at which point the water to acid ratio is so low that species not involving water become important. There is no reason to believe that the same would not be true of the other acids considered if experimental data were





available over the entire range. It has been shown that a multi-species model is better able to account for the acidity, since a single species model requires more water of hydration than the total amount of water present in solution. However, the model considering nothing but hydration requires unreasonably large values of the proton hydration number in dilute solution, which in sulfuric acid can be reduced somewhat by applying a correction for the activity coefficient of the indicator. Hence it appears that the activity coefficients of the indicators and possibly also the activity coefficients of their conjugate acids are important, especially in dilute solution. There is not sufficient data available at present to apply a proper correction, so the activity coefficient ratio  $f_B f_{H^+(H_2O)_n} / f_{BH^+}$  has been neglected.

The use of Raoult's law in a form which considers the species actually present rather than the stoichiometry of the system gives reasonable values for the hydration number of the electrolyte above about 3 to 4 m acid. These values are considerably lower than those obtained from the  $H_O$  function, but it is not known whether this is caused by error in one or both of the methods, or whether it reflects the measurement of related but different aspects of the same property. The failure of Raoult's law in dilute acid solution, plus the unexpected behavior of several other properties in about the same concentration range, are explained on the basis of changes in the structure of the solvent water. Specifically, the "flickering cluster" model of pure water has been used, and it is suggested that no clusters are present at acid concentrations greater than about 3 m.



An apparent maximum is observed in the proton hydration number as a function of acid concentration in sulfuric acid. Apparent maxima may or may not be present in monobasic acids. It has been shown that the maximum in sulfuric acid is not caused by hydration of the indicator or its conjugate acid, but it may be caused by variation of the activity coefficients of the hydrated species.

The Hammett acidity function,  $H_0$ , is probably the best acidity function for use in this type of calculation, possibly because of some fortuitous cancellation in the activity coefficient ratio. Four other acidity functions were tested in sulfuric acid.

Finally, it should perhaps be pointed out that this study has attempted to use data obtained from the behavior of organic molecules in order to gain some understanding of the behavior of the proton. Conversely, if the behavior of the proton were completely understood, the same study applied in reverse could yield additional information about the behavior of the organic species.





## BIBLIOGRAPHY

1. L. Zucker and L.P. Hammett, J. Am. Chem. Soc. 61, 2791 (1939).
2. J.F. Bunnett, J. Am. Chem. Soc. 83, 4956 (1961).
3. L.P. Hammett and A.J. Deyrup, J. Am. Chem. Soc. 54, 2721 (1932).
4. E. Wicke, M. Eigen and Th. Ackermann, Z. physik. Chem. (N.F.) 1, 340 (1954).
5. J.N. Brønsted, Rev. trav. chim. 42, 718 (1923).
6. J.N. Brønsted, Z. physik. Chem. A169, 52 (1934).
7. T.F. Young, L.F. Maranville and H.M. Smith, in "The Structure of Electrolytic Solutions", ed. W.J. Hamer, John Wiley and Sons, New York (1959), p. 35.
8. N. Bjerrum, Z. anorg. allgem. Chem. 109, 275 (1920).
9. E. Glueckauf and G.P. Kitt, Proc. Roy. Soc. A228, 322 (1955).
10. R.P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, N.Y. (1959), pp. 83-4.
11. K.N. Bascombe and R.P. Bell, Disc. Faraday Soc. 24, 158 (1957).
12. F.A. Long and W.F. McDevit, Chem. Rev. 51, 119 (1952).
13. P.A.H. Wyatt, Disc. Faraday Soc. 24, 162 (1957).
14. M.A. Paul and F.A. Long, Chem. Rev. 57, 1 (1957).
15. P.A.H. Wyatt, Trans. Faraday Soc. 56, 490 (1960).
16. T.F. Young and G.E. Walrafen, Trans. Faraday Soc. 57, 34 (1961).
17. G.C. Hood, O. Redlich and C.A. Reilly, J. Chem. Phys. 22, 2067 (1954).
18. G.C. Hood and C.A. Reilly, J. Chem. Phys. 32, 127 (1960).
19. E. Högfeldt, Acta Chem. Scand. 14, 1597 (1960).
20. E. Högfeldt, Acta Chem. Scand. 14, 1627 (1960).





21. E. Högfeldt, *Acta Chem. Scand.* 17, 785 (1963).
22. E. Högfeldt, *Sven. Kem. Tid.* 75, 63 (1963).
23. Reference (10), pp. 18-24.
24. H.S. Frank and M.W. Evans, *J. Chem. Phys.* 13, 507 (1945).
25. H.S. Frank and W.-Y. Wen, *Disc. Faraday Soc.* 24, 133 (1957).
26. H.S. Frank and A.S. Quist, *J. Chem. Phys.* 34, 604 (1961).
27. G. Nemethy and H.A. Scheraga, *J. Chem. Phys.* 36, 3382 (1962).
28. R.P. Marchi and H. Eyring, *J. Phys. Chem.* 68, 221 (1964).
29. W.F. Giauque, E.W. Hornung, J.E. Kunzler and T.R. Rubin, *J. Am. Chem. Soc.* 82, 62 (1962).
30. "International Critical Tables", McGraw Hill, New York (1928), Vol. III, pp. 54-8.
31. H. Harned and W.J. Hamer, *J. Am. Chem. Soc.* 57, 27 (1935).
32. K.N. Bascombe and R.P. Bell, *J. Chem. Soc.* 1096 (1959).
33. M.J. Jorgensen and D.R. Hartter, *J. Am. Chem. Soc.* 85, 878 (1963).
34. Reference (10), Chapter VII.
35. A.A. Zinov'ev, *Russ. Chem. Rev.* (English translation) 32, 268 (1963).
36. A.E. Markham, *J. Am. Chem. Soc.* 63, 874 (1941).
37. "Handbook of Chemistry and Physics", 43<sup>rd</sup> edition, Chemical Rubber Publishing Co., Cleveland, Ohio (1962), p. 2053.
38. R.A. Robinson and O.J. Baker, *Trans Proc. Roy. Soc. New Zealand* 76, 250 (1946). Quoted in *Chem. Abstr.* 41, 5000 d (1947).
39. J.N. Pearce and A.F. Nelson, *J. Am. Chem. Soc.* 55, 3075 (1933).
40. H.B. Dunford, unpublished results.
41. G.C. Hood and C.A. Reilly, *J. Chem. Phys.* 27, 1126 (1957).
42. R.E. Richards and J.A.S. Smith, *Trans Faraday Soc.* 47, 1261 (1951).



43. Y. Kakiuchi, H. Sheno, H. Matsu and K. Kigoshi, J. Chem. Phys. 19, 1069 (1951); J. Phys. Soc. Japan 7, 102 (1952).
44. A. Volmer, Ann. 440, 200 (1924).
45. R. Haase, H. Naas and H. Thumm, Z. physik. Chem. (N.F.) 37, 210 (1963).
46. E. Högfeldt, J. Inorg. Nucl. Chem. 17, 302 (1961).
47. M. Randall and L.E. Young, J. Am. Chem. Soc. 50, 989 (1928).
48. Landolt-Börnstein, Physikalisch-Chemische Tabellen, Julius Springer, Berlin (1960), Vol. II a, p. 372.
49. N.M. Milyaeva, Zhur. Neorg. Khim. 3, 2011 (1958).
50. E. Högfeldt and B. Bolander, Arkiv. Kemi 21, 161 (1963).
51. R.A. Robinson and R. H. Stokes, Trans. Faraday Soc. 45, 612 (1948).
52. J.G. Dawber and P.A.H. Wyatt, J. Chem. Soc. 3589 (1960).
53. R. Cini and N. Pernicone, Ann. Chem. (Rome) 49, 441 (1959).
54. P. Kebarle and A.M. Hogg, to be published in "Advances in Mass Spectrometry" (1964).
55. Reference (37), p. 1757.
56. R.H. Boyd, J. Am. Chem. Soc. 85, 1555 (1963).
57. L. Pauling, in "Symposium on Hydrogen Bonding, Ljubljand, 1957", ed. D. Hadzi, Pergamon Press, New York (1959), p. 1.
58. N. Deno and C. Perrizzolo, J. Am. Chem. Soc. 79, 1345 (1957).
59. D.N. Shaw, Nature 201, 922 (1964).
60. J.A. Pople, W.G. Schneider and H.J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York (1959), pp. 442-7.
61. J.C. Hindman, J. Chem. Phys. 36, 1000 (1962).
62. H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry", D. Van Nostrand Co., Princeton, New Jersey, 2<sup>nd</sup> ed. (1956), pp. 517-9.



63. E.M. Arnett, unpublished results.
64. F.A. Long and D. McIntyre, J. Am. Chem. Soc. 76, 5807 (1956).
65. W.F. McDevit and F.A. Long, J. Am. Chem. Soc. 74, 1773 (1952).
66. N.C. Deno, J.J. Jaurzelski and A. Schriesheim, J. Am. Chem. Soc. 77, 3044 (1955).
67. N.C. Deno, H.E. Berkheimer, W.L. Evans and H.J. Peterson, J. Am. Chem. Soc. 81, 2344 (1959).
68. H.S. Frank, J. Phys. Chem. 67, 1554 (1963).
69. R.A. Robinson and R.H. Stokes, "Electrolyte Solutions", Butterworths Publications Ltd., London (1955), p. 19.
70. E.M. Arnett and G.W. Mach, to be published (1964).
71. R.H. Boyd, J. Am. Chem. Soc. 83, 4288 (1961).
72. L. Michaelis and S. Granick, J. Am. Chem. Soc. 64, 1861 (1942).
73. E. Högfeldt, Acta Chem. Scand. 16, 1054 (1962).
74. R.W. Taft, J. Am. Chem. Soc. 82, 2965 (1960).
75. P.T. McTigue, Trans. Faraday Soc. 60, 127 (1964).





# APPENDIX

The following tables contain the molar concentration,  $C$ , and the weight per cent concentration corresponding to each of the rounded molalities,  $m$ , used in these calculations. The density,  $d$ , in g./ml. and the ratio of molar to molal concentrations are also tabulated. The values of the degree of dissociation,  $\alpha$ , are given for hydrobromic, hydrochloric and nitric acids. References to the sources of the density data and descriptions of the methods used to obtain  $\alpha$  are given in the Calculations section. All data refer to 25°C.

The molecular weights used are:

H <sub>2</sub> O	18.0153	H <sub>2</sub> SO <sub>4</sub>	98.0775	HClO <sub>4</sub>	100.458
HBr	80.917	HCl	36.461	HNO <sub>3</sub>	63.0139

TABLE 14.

## SUPPLEMENTARY DATA FOR SULFURIC ACID

$m$	$C$	Wt. %	$d$	$C / m$	$m / C$
0.0	0.00000	0.0000	0.9971	0.99707	1.0029
0.1	0.09938	0.9712	1.0036	0.99383	1.0062
0.2	0.19810	1.9238	1.0099	0.99048	1.0096
0.3	0.29609	2.8582	1.0160	0.98697	1.0132
0.4	0.39331	3.7750	1.0219	0.98327	1.0170
0.5	0.48986	4.6746	1.0278	0.97970	1.0207
0.6	0.58576	5.5576	1.0337	0.97626	1.0243
0.7	0.68093	6.4244	1.0395	0.97275	1.0280
0.8	0.77542	7.2754	1.0453	0.96925	1.0317
0.9	0.86914	8.1110	1.0510	0.96570	1.0355
1.0	0.96228	8.9318	1.0566	0.96226	1.0392
1.5	1.4172	12.825	1.0838	0.94481	1.0584
2.0	1.8554	16.399	1.1097	0.92771	1.0779
2.5	2.2771	19.691	1.1342	0.91081	1.0979
3.0	2.6826	22.734	1.1573	0.89420	1.1183
3.5	3.0731	25.555	1.1794	0.87803	1.1389
4.0	3.4483	28.177	1.2003	0.86207	1.1600
4.5	3.8094	30.621	1.2201	0.84652	1.1813



TABLE 14. -- Continued

m	C	Wt. %	d	C / m	m / C
5.	4.1559	32.903	1.2388	0.83117	1.2031
6.	4.8108	37.046	1.2736	0.80178	1.2472
7.	5.4175	40.707	1.3053	0.77394	1.2921
8.	5.9813	43.966	1.3343	0.74765	1.3375
9.	6.5076	46.885	1.3613	0.72306	1.3830
10.	6.9994	49.515	1.3864	0.69992	1.4287
11.	7.4602	51.896	1.4099	0.67819	1.4745
12.	7.8916	54.064	1.4316	0.65763	1.5206
13.	8.2977	56.044	1.4521	0.63828	1.5667
14.	8.6789	57.861	1.4711	0.61992	1.6131
15.	9.0383	59.533	1.4890	0.60256	1.6596
16.	9.3765	61.078	1.5056	0.58602	1.7064
17.	9.6960	62.509	1.5213	0.57034	1.7533
18.	9.9978	63.839	1.5360	0.55543	1.8004
19.	10.284	65.077	1.5499	0.54127	1.8475
20.	10.554	66.234	1.5628	0.52770	1.8950
22.	11.055	68.331	1.5867	0.50248	1.9901
25.	11.717	71.031	1.6179	0.46868	2.1336
30.	12.633	75.634	1.6601	0.42110	2.3747
35.	13.367	77.440	1.6929	0.38191	2.6184
40.	13.964	79.688	1.7186	0.34908	2.8646
45.	14.453	81.528	1.7387	0.32118	3.1135
50.	14.860	83.062	1.7546	0.29720	3.3647
60.	15.489	85.475	1.7773	0.25816	3.8736
70.	15.946	87.286	1.7917	0.22778	4.3901
80.	16.290	88.696	1.8013	0.20362	4.9109
90.	16.550	89.824	1.8081	0.18399	5.4350
100.	16.774	90.747	1.8129	0.16774	5.9616
150.	17.422	93.635	1.8248	0.11614	8.6100
200.	17.743	95.149	1.8289	0.088714	11.272
300.	18.050	96.713	1.8311	0.060167	16.620
400.	18.207	97.514	1.8312	0.045515	21.970
500.	18.296	98.002	1.8310	0.036590	27.329
1000.	18.462	98.991	1.8292	0.018462	54.165
	18.613	100.000	1.8255	-	-



TABLE 15.  
SUPPLEMENTARY DATA FOR PERCHLORIC ACID

m	C	Wt. %	d	C / m
0.0	0.00000	0.0000	0.99707	0.99707
0.1	0.09926	0.9946	1.00263	0.99266
0.2	0.19765	1.9696	1.00811	0.98827
0.3	0.29518	2.9256	1.01359	0.98297
0.4	0.39184	3.8631	1.01896	0.97960
0.5	0.48768	4.7827	1.02436	0.97536
0.6	0.58269	5.6848	1.02968	0.97115
0.7	0.67687	6.5701	1.03496	0.96695
0.8	0.77024	7.4388	1.04018	0.96281
0.9	0.86280	8.2916	1.04535	0.95866
1.0	0.95462	9.1287	1.05053	0.95464
1.5	1.4023	13.096	1.07575	0.93486
2.0	1.8319	16.730	1.09998	0.91595
2.5	2.2446	20.073	1.12333	0.89784
3.0	2.6418	23.158	1.14597	0.88058
3.5	3.0238	26.014	1.16772	0.86396
4.0	3.3928	28.665	1.18905	0.84822
4.5	3.7486	31.132	1.20962	0.83302
5.	4.0921	33.435	1.22951	0.81842
6.	4.7454	37.607	1.26763	0.79091
7.	5.3596	41.287	1.30407	0.76565
8.	5.9343	44.557	1.33794	0.74180
9.	6.4790	47.482	1.37075	0.71990
10.	6.9879	50.114	1.40079	0.69880
11.	7.4741	52.495	1.43030	0.67946
12.	7.9281	54.659	1.45711	0.66068
13.	8.3606	56.634	1.48301	0.64313
14.	8.7676	58.444	1.50703	0.62625
15.	9.1498	60.110	1.52916	0.60998
16.	9.5132	61.647	1.55026	0.59457
55.508	14.89 g	84.794	1.764 g	0.2682 g
	17.50 g	100.000	1.758 g	-

g Estimated values.





TABLE 16.

## SUPPLEMENTARY DATA FOR HYDROBROMIC ACID

m	C	Wt. %	d	C / m	$\alpha$
0.0	0.00000	0.0000	0.9971	0.99707	1.0000
0.1	0.09946	0.8027	1.0027	0.99463	1.0000
0.2	0.19843	1.5925	1.0082	0.99216	1.0000
0.3	0.29694	2.3700	1.0138	0.98979	1.0000
0.4	0.39494	3.1352	1.0193	0.98736	1.0000
0.5	0.49242	3.8885	1.0247	0.98483	1.0000
0.6	0.58945	4.6302	1.0301	0.98241	1.0000
0.7	0.68600	5.3606	1.0355	0.98001	1.0000
0.8	0.78201	6.0798	1.0408	0.97751	1.0000
0.9	0.87762	6.7882	1.0461	0.97514	1.0000
1.0	0.97257	7.4860	1.0513	0.97257	1.0000
1.5	1.4411	10.824	1.0773	0.96070	1.0000
2.0	1.8981	13.929	1.1026	0.94903	1.0000
2.5	2.3434	16.825	1.1270	0.93737	1.0000
3.0	2.7798	19.533	1.1515	0.92662	1.0000
3.5	3.2048	22.070	1.1750	0.91566	1.0000
4.0	3.6202	24.452	1.1980	0.90505	1.0000
4.5	4.0261	26.693	1.2205	0.89469	1.0000
5.	4.4232	28.804	1.2425	0.88464	1.0000
6.	5.1926	32.682	1.2856	0.86542	1.0000
7.	5.9267	36.160	1.3262	0.84666	0.9997
8.	6.6286	39.296	1.3649	0.82856	0.9982
9.	7.3022	42.138	1.4022	0.81136	0.9884
10.	7.9415	47.726	1.4368	0.79415	0.9772
11.	8.5590	47.092	1.4707	0.77808	0.9683
12.	9.1449	49.264	1.5021	0.76208	0.9602
13.	9.7080	51.264	1.5323	0.74677	0.9537
14.	10.247	53.113	1.5610	0.73191	0.9482



TABLE 17.

## SUPPLEMENTARY DATA FOR HYDROCHLORIC ACID

m	C	Wt. %	d	C / m	$\alpha$
0.0	0.00000	0.00000	0.9971	0.99707	1.0000
0.1	0.09952	0.36328	0.9989	0.99522	0.9995
0.2	0.19867	0.72394	1.0006	0.99334	0.9990
0.3	0.29747	1.0820	1.0024	0.99156	0.9986
0.4	0.39588	1.4374	1.0041	0.98970	0.9981
0.5	0.49397	1.7904	1.0059	0.98794	0.9976
0.6	0.59160	2.1409	1.0076	0.98599	0.9971
0.7	0.68891	2.4888	1.0093	0.98416	0.9966
0.8	0.78585	2.8342	1.0110	0.98231	0.9962
0.9	0.88244	3.1772	1.0127	0.98048	0.9957
1.0	0.97866	3.5178	1.0143	0.97866	0.9952
1.5	1.4542	5.1856	1.0225	0.96945	0.9868
2.0	1.9203	6.7966	1.0302	0.96014	0.9780
2.5	2.3776	8.3537	1.0377	0.95103	0.9699
3.0	2.8259	9.8595	1.0450	0.94196	0.9618
3.5	3.2658	11.316	1.0522	0.93310	0.9538
4.0	3.6975	12.728	1.0592	0.92438	0.9460
4.5	4.1212	14.094	1.0661	0.91583	0.9383
5.	4.5360	15.419	1.0726	0.90720	0.9308
6.	5.3433	17.950	1.0854	0.89055	0.9161
7.	6.1200	20.333	1.0974	0.87428	0.9020
8.	6.8681	22.582	1.1089	0.85852	0.8884
9.	7.5879	24.707	1.1198	0.84309	0.8753
10.	8.2808	26.719	1.1300	0.82809	0.8628
11.	8.9474	28.626	1.1396	0.81340	0.8507
12.	9.5969	30.436	1.1497	0.79973	0.8389
13.	10.205	32.157	1.1571	0.78499	0.8279
14.	10.799	33.794	1.1651	0.77136	0.8171
15.	11.371	35.355	1.1727	0.75808	0.8067
16.	11.922	36.844	1.1798	0.74509	0.7968
17.	12.452	38.266	1.1865	0.73250	0.7871
18.	12.980	39.624	1.1943	0.72108	0.7776



TABLE 18.

## SUPPLEMENTARY DATA FOR NITRIC ACID

m	C	Wt. %	d	C / m	$\alpha$
0.0	0.00000	0.0000	0.9971	0.99707	1.0000
0.1	0.09941	0.6262	1.0004	0.99414	0.9963
0.2	0.19824	1.2446	1.0037	0.99122	0.9926
0.3	0.29650	1.8553	1.0070	0.98832	0.9890
0.4	0.39417	2.4586	1.0103	0.98542	0.9853
0.5	0.49126	3.0544	1.0135	0.98251	0.9816
0.6	0.58778	3.6430	1.0167	0.97963	0.9778
0.7	0.68373	4.2246	1.0198	0.97675	0.9742
0.8	0.77911	4.7991	1.0230	0.97389	0.9704
0.9	0.87393	5.3668	1.0261	0.97103	0.9668
1.0	0.96818	5.9278	1.0292	0.96818	0.9632
1.5	1.4314	8.6357	1.0445	0.95429	0.9448
2.0	1.8813	11.192	1.0592	0.94065	0.9263
2.5	2.3185	13.609	1.0735	0.92740	0.9080
3.0	2.7432	15.898	1.0873	0.91440	0.8895
3.5	3.1557	18.069	1.1005	0.90163	0.8711
4.0	3.5562	20.131	1.1131	0.88906	0.8530
4.5	3.9453	22.092	1.1253	0.87673	0.8356
5.	4.3234	23.958	1.1371	0.86468	0.8175
6.	5.0480	27.435	1.1594	0.84133	0.7834
7.	5.7330	30.608	1.1803	0.81899	0.7498
8.	6.3811	33.515	1.1997	0.79765	0.7168
9.	6.9919	36.188	1.2175	0.77688	0.6851
10.	7.5649	38.655	1.2332	0.75648	0.6541
11.	8.1055	40.938	1.2476	0.73686	0.6241
12.	8.6164	43.059	1.2610	0.71803	0.5950
13.	9.0998	45.030	1.2734	0.69998	0.5674
14.	9.5583	46.870	1.2850	0.68272	0.5410
15.	9.9920	48.591	1.2958	0.66613	0.5158
16.	10.401	50.204	1.3055	0.65006	0.4911
17.	10.788	51.719	1.3144	0.63460	0.4680
18.	11.154	53.145	1.3226	0.61969	0.4456
19.	11.503	54.488	1.3302	0.60540	0.4243
20.	11.833	55.757	1.3373	0.59164	0.4039
22.	12.446	58.094	1.3500	0.56574	0.3660
25.	13.260	61.170	1.3659	0.53039	0.3144
30.	14.384	65.403	1.3859	0.47947	0.2427
35.	15.297	68.803	1.4010	0.43707	0.1890
40.	16.050	71.595	1.4126	0.40125	0.1536
45.	16.681	73.928	1.4218	0.37068	0.1284
50.	17.218	75.907	1.4293	0.34435	0.1100





TABLE 18. -- Continued

m	C	Wt. %	d	C / m	$\alpha$
60.	18.081	79.083	1.4407	0.30134	0.0821
70.	18.747	81.519	1.4491	0.26781	0.0633
80.	19.273	83.446	1.4554	0.24092	0.0495
90.	19.701	85.010	1.4603	0.21891	0.0394
100.	20.052	86.304	1.4641	0.20053	0.0328
150.	21.171	90.432	1.4752	0.14114	0.0151
200.	21.762	92.648	1.4801	0.10881	0.0088
300.	22.376	94.976	1.4846	0.074587	0.0039
400.	22.699	96.184	1.4871	0.056746	0.0024
500.	22.899	96.924	1.4887	0.045798	0.0019
1000.	23.342	98.438	1.4942	0.023342	0.0009
	23.868	100.000	1.5040	-	0.0000







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